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DETERMINATIONS OF LACTOSE IN MILKS BY OPTICAL METHODS.

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The usual method of determining milk sugar by evaporating the sample to dryness, and extracting the sugar with alcohol after exhausting with ether, requires a great deal of time and labor. If some reliable optical method could be devised, the determination of the lactose in milk would be the work of only a few minutes. The difficulties which are encountered in seeking for such a method are numerous and serious, so much so that little credit has heretofore been given to any of the processes of optical analysis in use. In the following paper I will give the results which have been obtained under my direction in the study of this problem. The optical work collected in the following tables was done chiefly by my assistants, Messrs. G. L. Spencer and C. A. Crampton; the alcohol extractions were made by Mr. A. E. Knorr, and the nitrogen estimation by Messrs. Fuller and Trescott.

Specific Rotatory Power of Milk Sugar.

Crystallised milk sugar when first dissolved possesses a higher rotatory power than it has in the milk from which it was derived. This increased optical activity may be compared with the original by the ratio 8 : 5, nearly. After the solution has stood for twelve to twenty hours, or immediately on boiling it, this extra rotatory

power is lost. In estimating the specific rotatory power of milk sugar the numbers given always refer to the constant and not the transient gyratory property.

Among the earliest numbers assigned to the rotation of lactose are those of Poggiale $(a)_D = 54.2$ and Erdmann $(a)_D = 51.5$, (Sucrose $(a)_D = 66.5$). Biot[1] places this number for lactose at 60.23, and Berthelot[2] at 59.3 for the transition tint $(a)_j$. Hoppe-Seyler, in his "Handbuch der physiologisch-chemischen Analyse," gives this number at $(a)_j = 58.2$. Since the ratio of $(a)_D$ to $(a)_j$ is 1 : 1.1306, the above numbers become for Biot $(a)_D = 53.27$, for Berthelot $(a)_D = 52.47$, and Hoppe-Seyler $(a)_D = 51.48$. Hesse[3] observed the rotation number to be $(a)_D = 52.67$, when the solution contained 12 g. per 100 cc. and the temperature was 15°. On the other hand, when the concentration is only 2 g. per 100 cc. the number assigned is $(a)_D = 53.63$. It appears from this that the specific rotation power of a solution of milk sugar diminishes with the increase of its concentration, and this view is adopted by Landolt, Tollens and Schmidt.

The following general formula[4] is used to correct the reading of the polariscope for concentration of solution:

$$(a)_D = 54.54 - .5575\, c + .05475\, c^2 - .001774\, c^3,$$

in which c = number grams sugar in 100 cc. solution. These observations are contradicted by the work of Schmoeger,[5] who, in an elaborate series of experiments, using instruments of different construction and observing all necessary precautions, found the rotation number of lactose sensibly constant for all degrees of concentration up to the saturation point. In 32 series of investigations, in which the degree of concentration gradually increases from $c = 2.3554$ to $c = 36.0776$, and in which a constant temperature of 20° was maintained, the variations in the numbers obtained were always within the limits of error of observation. The mean of all these numbers fixes the value of $(a)_D$ at 52.53.

According to Schmoeger, variations in temperature have far more to do with changes in rotatory power than differences of concentration. The value of $(a)_D$ falls as the temperature rises.

[1] Compt. rend. **42**, 349.
[2] Dict. de Chem. par Ad. Würtz **2**, 2d part, p. 188.
[3] Annal. Chem. u. Pharm. **176**, 98.
[4] Tucker, Sugar Analysis, 91.
[5] Berichte der deutsch. chem. Gesell. 1880, 1922 et seq.

Under 20° the disturbing influence of temperature is greater than above 20°. At the latter degree $(a)_D$ varies inversely about .075 for each 1° change of temperature. Pellet and Biard,[1] as a result of their observations, fix the rotatory power of milk sugar at 58.94 for $(a)_j$ ($(a)_D = 52.12$).

After a careful review of the methods used in the above *resumé* and the numbers determined by them, I am inclined to accept the mean obtained by Schmoeger as the one entitled to the greatest credit. It also has the advantage of being almost the mean of all the various numbers which have been assigned as the specific rotating power of lactose, viz.

Poggiale, . .	54.2
Erdmann, . .	51.5
Biot, . . .	53.27
Berthelot, . .	52.47
Hoppe-Seyler, .	51.48
Hesse, . . .	52.67
" . . .	53.63
Schmoeger, . .	52.53
Pellet and Biard, .	52.12
Mean,	52.65

In the present state of our knowledge, therefore, the specific rotatory power of milk sugar should be taken at $(a)_D = 52.5$. I propose, at an early date, to make a careful study of this subject, in order to fix, if possible, an exact number for the expression of the rotating power, and to examine the conflicting evidence respecting the influence of the degree of concentration on the same. The estimation of lactose in milk by the polariscope is rendered difficult also by the presence in milk of various albumens—all of which turn the plane of polarisation to the left. As will be seen by the data given further along, the ordinary method of removing these albumens, viz. by a solution of basic lead acetate, is far from being perfect. If, therefore, a portion of the albumen be left in the liquid submitted to polarisation, the rotation to the right will be diminished by its presence.

Hoppe-Seyler[2] assigns as the rotation power of egg albumen $(a)_D = -35.5$, and for serum albumen $(a)_D = -56$. Both acids

[1] Bull. de l'Assoc. des Chimistes **1**, 5, 171 et seq. [2] Würtz, Dictionnaire de Chimie **1**, 91.

and alkalies seem to increase the rotating power, which may with acetic acid reach $(a)_D = -71$.

Fredericq[1] gives the rotation number for blood serum for the rabbit, cow and horse at $(a)_D = -57.3$, and for the dog at -44. Paraglobulin, according to the same author, has a rotation number $(a)_D = -47.8$.

Milk albumen[2] has the following numbers assigned to it:

Dissolved in $MgSO_4$ sol.	$(a)_D = -80$
" " dil. HCl.	" $= -87$
" " dil. NaOH sol.	" $= -76$
" " strong KOH sol.	" $= -91$

The hydrates of albumen[3] have rotation powers which vary from $(a)_D = -71.40$ to $(a)_D = -79.05$. From the chaotic state of knowledge concerning the specific rotating power of the various albumens, it is impossible to assign any number which will bear the test of criticism. For the purposes of this paper, however, this number may be fixed at $(a)_D = -70$ for the albumens which remain in solution in the liquids polarised for milk sugar.

The phenomenon of "birotation" in milk sugar has already been noticed. The problem of analysis of this sugar is, however, still further complicated by the facts pointed out by Schmoeger[4] and Erdmann[5] that when milk is rapidly evaporated in a plain dish the sugar is left in the anhydrous state, and that this sugar in fresh solutions exhibits the phenomenon of "half rotation." When such sugar is extracted with alcohol and re-evaporated, it, doubtless, is still anhydrous. But in the calculation of results this sugar is generally estimated as containing water of crystallisation, and thus an error, which Schmoeger reckons at as much as .2 per cent., is introduced into the results. This fact, not well recognised, combined with the knowledge that in the process of evaporation many particles of sugar must be occluded by the hardening caseine, tends to throw doubt upon the accuracy of estimating the sugar by the extraction method.

The work which I undertook had for its object the determination of the best method of preparing the milk-sugar solution for

[1] Compt. rendus, 93-465.
[2] Hoppe-Seyler in Handbook of the Polariscope, Landolt, p. 248.
[3] Kühne and Chittenden, Am. Chem. Journal **6**, 45.
[4] Ber. d. deutsch. chem. Gesell, 1880, 1915 et seq.; 1881, 212 et seq.
[5] Ber. d. deutsch. chem. Gesell, 1880, 2180 et seq.

the polariscope, and a comparison of the numbers obtained by this instrument with those given by the ordinary process of extraction.

The reagents used for removing the albumens were:

(1) Saturated solution basic lead acetate, sp. gr. 1.97.

(2) Nitric acid solution of mercuric nitrate diluted with an equal volume of water.

(3) Acetic acid, sp. gr. 1.040, containing 29 per cent. $HC_2H_3O_2$.

(4) Nitric acid, sp. gr. 1.197, containing 30 per cent. HNO_3.

(5) Sulphuric acid, sp. gr. 1.255, containing 31 per cent. H_2SO_4.

(6) Saturated solution sodium chloride.

(7) Saturated solution magnesium sulphate.

(8) Solution of mercuric iodide in acetic acid; formula[1] KI, 33.2 g. $HgCl_2$, 13.5 g.

Strong $HC_2H_3O_2$, 20.0 cc.
Water, 640 cc.

Alcohol, ether and many solutions of mineral salts, hydrochloric and other acids were also tried as precipitants for albumen, but none of them presented any advantages which would make a detailed account of the experiments of any interest.

Table No. I.

This table contains a record of the experiments which led to the adoption of 1 cc. acetate of lead solution, or 1 cc. acid mercuric nitrate, as the best amount of each for 50 cc. of milk.

Nearly all the polarisations were made in a 400 mm. tube. From two to four observations were made with each sample. An average of these readings was taken for each determination. In the calculations the value of $(a)_D$ was taken at 53 instead of 52.5, the number which subsequent investigations have led me to believe more exact. The instrument employed was a "Laurent Large Model" polariscope.

In all cases the volume of the solution was corrected for the volume of the precipitated caseine. This volume was assumed to occupy 2 cc. for each 50 cc. milk.

Since in the Laurent instrument the weight of sucrose in 100 cc. to read even degrees on the scale is 16.19 g. $[(a)_D = 66.67]$, it follows that the weight of lactose in 100 cc. to read one degree on the

[1] Journal de Pharmacie et de Chimie, Aug. 1884, 108.

TABLE I.

Reagents Employed in Precipitating Albumens.

No.	Per cent. lactose estimated by alcohol.	Pb 1 cc.	Pb 2 cc.	Pb 3 cc.	Pb 4 cc.	Pb 5 cc.	A 5 cc.	Other Reagents.
		Per cent. Lactose.						
1	4.57				10 cc.	3.67	4.23	
2	4.52				2.45	3.57	4.14	
3	4.46	4.48					3.57	
4	3.92	4.19				3.35		
5	4.35		3.55				4.32	
6	3.71	4.01					3.00	
7	4.10	4.63 4.96 H					4.44 4.68 H	
8	4.16	4.29 4.33					3.80 3.67 H	
9	4.48	4.59 4.58 H					4.04 4.12 H	
10	4.10	4.12 H					3.47 H	H_2SO_4
11	4.80	4.87 H			(4 cc.)		4.44 H	4 cc. 5 cc. 6 cc. 8 cc.
12	4.77	5.02 H	4.82 H	4.50 H	4.31 H			4.70 H 4.76 H 4.76 H 4.78 H
13	4.25	4.25	3.75	3.38	3.38			3 cc. 3.97 3.89
14	4.22	4.90 H	4.58 H					HNO_3
15	3.14	4.40 4.32 H						4.68 H 4.66 H 4.50 H
16	3.30	4.43 H						
17	4.72	4.45	4.18	3.87	3.65	3.26		3.98 3.96 3.98 3.88 3.88 H
18	4.88	4.87 4.87 H					4.37 4.25	4.27 (5 cc.) 4.43 H_2SO_4
19	4.31	4.71 4.86 H					4.43 4.43 H	4.51 4.59 4.79 H 4.59 H
20	4.39	4.11						
21	4.70	4.17						
22	4.96	4.93 4.97 H					4.45 4.43 H	4.69 4.67 H
23	4.60	4.41 4.45					3.86 3.86	3.90 3.94 3.90 4.10
24	4.74	4.41 4.45 H					4.21 4.35 H	4.32 4.32 4.44 H 4.55 H
25	4.59	4.33 4.37 H	NaCl	1 cc. MR			3.94 3.93 H	4.03 3.98 4.10 H 4.10 H
26	4.39		4.29 H	4.29 H				
27	4.60	4.18 H		4.66				
28	4.26	3.67 H		4.09				

scale for each per cent. lactose present would be 16.19, $x = 53$; 66.67, $x = 20.37$.

If 52.5 be taken as the value of $(a)_D$ for lactose, then $x = 20.56$.

In table No. I, A indicates acetic acid, Pb basic acetate of lead, MR acid mercuric nitrate, etc. The letters C and H indicate the temperature; C denoting the ordinary temperature of the room, and H that the sample was heated to 100° and cooled before filtering.

The numbers obtained by extraction with alcohol are taken as the basis of comparison, not because I believe them to be more reliable, but because that method is the one generally employed in the estimation of milk sugar.

In the alcohol extraction the milk was evaporated to dryness in a thin glass capsule, the dish and dried residue pulverised in a mortar, washed with ether into a continuous extraction apparatus, exhausted with ether, and then with 80 per cent. alcohol for ten hours.

Duplicate analyses are indicated in the table by the small brackets.

Remarks on Table I.

The results obtained by using various other reagents for the precipitation of the caseine, viz. $MgSO_4$, $CuSO_4$, HCl, etc., have not been entered in the table. In none of these cases was there sufficient encouragement to warrant an extended trial. In most cases the precipitation was slow or imperfect, and the filtration difficult.

One important fact should not be overlooked, viz. that any excess of basic plumbic acetate causes a rapid decrease in the rotatory power of the solution; whether this decrease is due to precipitation of the sugar or solution of the albumens does not clearly appear. Illustrations of this decrease are seen in analyses 2, 12, 13 and 17.

It seems to make little difference whether the precipitation is made hot or cold. The question of temperature is set forth in greater detail in the next table. From all the experiments made it clearly appeared that the best optical results are obtained by the use of a minimum quantity of basic lead acetate, or of either the acid mercuric nitrate or iodide. For 50 to 60 cc. of milk, 1 cc. of the lead acetate or mercuric nitrate solution of the strength noted,

and 25 cc. of the mercuric iodide solution are the proper quantities. It makes no difference, however, if a large excess of the two latter reagents is employed. Of the three the last is to be preferred.

Table No. II.

In this table will be found the results of the comparative determinations of milk sugar by extraction with alcohol, by precipitation with 1 cc. basic lead acetate, and the same with 1 cc. acid mercuric nitrate, hot and cold, to each 60 cc. of milk.

In many of the analyses the large differences in results by the three methods show a fault of manipulation, but all the results have been given without selection.

Table II.

No.	Extract by Alcohol.	Reagents Employed. C. Pb 1 cc.	H. Pb 1 cc.	C. MR 1 cc.	H. MR 1 cc.
			Percentage of Milk Sugar.		
1	4.55		4.74		4.92
2	4.10		4.22		4.50
3	4.51	4.54	4.22	4.68	4.62
4	4.36	4.55	4.53	4.89	4.90
5	4.05	4.14	4.09	4.48	4.39
6	3.84		3.84	3.98	3.98
7	4.52	4.67	4.73	5.01	5.00
8	4.25	4.21	4.26		4.51
9	4.45	4.61	4.54	4.87	4.87
10	4.92	5.20	5.22	5.43	5.47
11	3.84		3.72	4.00	3.96
12	4.53	4.61	4.64	4.87	4.85
13	4.57	4.54	4.55	4.91	4.84
14	4.66	4.29	4.45		4.63
15	4.17	3.65	3.75	3.95	3.87
16	5.02	4.66	4.64	4.86	4.86
17	4.68	4.03	3.94	4.39	4.37
18	4.23	3.82	3.89	4.08	4.02
19	4.96	4.70	4.84	5.04	5.04
20	4.85	4.39	4.41	4.53	4.65
21	4.63	4.47	4.47	4.69	4.67
22	4.47	4.39	4.45	4.67	4.71
23	4.46	4.23	4.31	4.65	4.63
24	4.47	4.59	4.67	5.01	4.95

No.	Extract by Alcohol.	C. Pb 1 cc.	H. Pb 1 cc.	C. MR 1 cc.	H. MR 1 cc.
25	4.40	4.41	4.55	4.45	
26	4.85	4.67	4.73	4.97	
27	4.45	4.21	4.33	4.57	
28	4.44	3.98	4.10	4.28	
29	4.10	4.21		4.55	
30	4.38	5.57	4.69	4.89	
31	4.20	4.21	4.37	4.57	
32	4.69	4.59	4.67	4.89	
33	4.52	4.27	4.41	4.41	
34	4.37	4.65	4.93	4.93	
35	4.52	4.27	4.41	4.56	
36	4.88	4.83	4.93	5.17	
37	4.61	4.30	4.43	4.57	
38	4.79	4.59	4.67	4.91	
39	4.67	4.26	4.41	4.51	
40	4.79	4.64	4.74	4.94	
41	3.95	4.10	4.26	4.38	
42	4.00	4.61	4.61	4.77	
43	4.63	4.24	4.37	4.57	
44	4.77	4.64	4.70	4.94	
45	4.85		4.53	4.73	
46	4.71		4.67	4.93	
47	4.34	4.06	4.12	4.40	
48	4.05	4.67	4.77	4.83	
49	3.67	4.12	4.18	4.36	
50	3.78	4.58	4.62	4.82	
51	4.19	4.27	4.57	4.53	
52	3.83	4.68	4.78	4.97	
53	3.86	3.97	4.07	4.21	
54	4.59	4.59	4.61	4.83	
55	4.02	4.26	4.36	4.40	
56	4.36	4.62	4.76	4.94	
57	4.20	4.18	4.28	4.48	
58	4.09	4.52	4.56	4.74	
59	4.09		4.28	4.46	
60	4.12		4.49	4.81	
61	4.20		4.33	4.41	
62	4.45		4.25	4.77	
63	4.33		4.09	4.37	
64	4.62		4.33	4.99	
Mean,	4.33	4.34	4.38	4.58	4.63

In the following table will be found the percentage of milk sugar obtained by using varying quantities of the mercuric iodide reagent,

and a comparison of the results obtained with those given by the use of acid mercuric nitrate and basic plumbic acetate.

TABLE III.

Reagents Employed.

No.	PbA	MR	Mercuric Iodide. 20 cc.	26 cc.	30 cc.	35 cc.
			Percentage of Milk Sugar.			
1	4.28	4.48	4.56	4.56		
2	4.46	4.57	4.62	4.66		
3	4.37	4.65	4.63	4.63	4.60	4.65
4	4.37	4.53	4.60	4.53	4.63	4.60
5	4.38	4.63	4.50	4.53	4.53	4.59
6	4.33	4.67	4.43	4.53	4.60	4.66
7	4.30	4.67	4.67	4.67	4.59	4.57
8	4.33	4.59	4.50	4.53	4.50	4.59
9	4.27	4.60	4.63	4.60	4.66	4.66
	4.34	4.60	4.57	4.58	4.61	4.62

Albumen remaining in Filtrate from Lead Acetate and Mercuric Iodide Solutions.

From the fact that the polariscopic readings show that solutions of milk prepared with lead acetate have a lower rotating power than those prepared with mercury salts, it is to be inferred that the lead reagent either leaves certain soluble and transparent kinds of albumen in solution, or else dissolves a portion of those which are at first precipitated. To test the accuracy of this supposition a few analyses were made to determine the amount of albumen left in the filtrate from the lead and mercury reagents. At the same time different quantities of the mercuric iodide solution were used, in order to determine the amount which would give the best results. For 60 cc. milk the quantity of mercuric iodide to be used should be 25 to 30 cc.

In the following table will be found the percentages of albumen in the whey after precipitating with the reagents noted and filtering. Ten cc. of the filtrate were evaporated to dryness in a thin glass dish, and the dried residue (with the glass) burned with soda lime. The calculated nitrogen was then multiplied by 6.25 and the product taken as the percentage of albumen.

TABLE IV.

Per cent. albumen in filtrate from PbA.	Per cent. albumen in filtrate from HgI_2. 15 cc.	Per cent. albumen in filtrate from HgI_2. 20 cc.	Per cent. albumen in filtrate from HgI_2. 25 cc.	Per cent. albumen in filtrate from HgI_2. 30 cc.	Per cent. albumen in filtrate from HgI_2. 35 cc.
.0865	.195	.0865	.0865	.0562	.0865
.113	.0674	.0865	.0865	.0865	.0865
.113	.0674	.0562	.113	.0562	.0312
.0865	.0674	.0562	.113	.0562	.0562
.113	.0674	.0562	.0312	.0865	0.562
.113	.009	.0865	.03	.0862	.1412
.113		.1412	.113	.1412	.0562
.195		.1412	.113	.1412	.1412
.113		.1412	.0865	.1412	.0865
.1412		.113	.1412	.113	.0865
.113		.1362	.009		
		.125			
		.009			
		.009			
Mean, .1182	.0789	.0888	.0839	.0964	.0828

In table No. V will be found percentages of albumen remaining in filtrate from lead acetate precipitation of forty-two samples taken from those represented in table No. II. From these two tables it is at once seen that the quantity of laevo-rotatory matter remaining in milk after treatment with basic lead acetate is much greater than in those samples treated with the two mercuric salts. This explains at once the higher per cent. of milk sugar obtained by using the last-named reagents, and shows that the use of lead acetate as a clarifying agent must be abandoned.

Per cent. Albumen after Precipitation by Lead Acetate.

No.	Pr ct.	No.	Pr ct.	No.	Pr ct.
1	.250	15	.271	29	.350
2	.306	16	.237	30	.374
3	.135	17	.237	31	.329
4	.272	18	.169	32	.305
5	1.34	19	.103	33	.305
6	.239	20	.271	34	.237
7	.301	21	.237	35	.305
8	.305	22	.271	36	.339
9	.237	23	.235	37	.237
10	.339	24	.271	38	.374
11	.271	25	.237	39	.203
12	.305	26	.237	40	.373
13	.267	27	.271	41	.305
14	.237	28	.339	42	.339
				Mean,	.278

Comparison of Results obtained by Extraction with Alcohol and Polarisation.

By consulting table II it will be seen that the percentage of sugar obtained by extraction with alcohol is practically the same as that got by polarisation of the lead acetate filtrate.

Thus, the mean percentage of sugar by alcohol (65 analyses) is 4.32; by lead acetate, cold (53 analyses) is 4.34; by lead acetate, hot (64 analyses) is 4.38; by mercuric nitrate, cold (61 analyses) is 4.58; by mercuric nitrate, hot (24 analyses) is 4.63.

If now the milk sugar, as has already been intimated, exists in an anhydrous state after extraction with alcohol, the percentage of it after the addition of the molecule of water would be increased. Thus molecular weight of anhydrous milk sugar 342 : mol. wt. of the hydrous from $360 = 4.38 : x$, whence the value of $x = 4.61$. This agrees very nearly with the number obtained by acid mercuric nitrate.

By a study of table V it is found that mercuric iodide gives nearly the same rotatory power as mercuric nitrate, and also that by combustion the filtrates from the milks clarified by lead acetate contain more albumen than those prepared with mercuric iodide. There is, therefore, every reason for believing that the numbers given by the mercury salts are nearer the truth than those from the lead.

It may be urged that the increased rotatory power observed by the mercury salts is due to the conversion, by the dilute acids, of a part of the lactose into galactose, which has a rotatory power greater than that of milk sugar. But when it is remembered that the quantity of acid introduced is extremely minute, that the samples need not be warmed, that they can be filtered and polarised within a few minutes of the time of the introduction of the reagents, the suggestion is seen to be of no force.

For example, in the acid mercuric nitrate it was found that the percentage of sugar was the same whether one, five or ten cc. of the reagent were employed, and whether it was polarised immediately or after heating and cooling. It is evident that one cc. of the reagent, containing less than a half cc. of nitric acid and diluted in 100 cc. of liquid, could not exert any notable effect on the rotatory power of the solution.

In the mercuric iodide solution 20 cc. of acetic acid are used for every 660 cc. of the reagent.

Thirty cc. of this reagent contain, therefore, about one cc. of acid. This in 100 cc. of liquid, immediately filtered and polarised, could not affect in any marked degree the rotatory power.

Since combustion with soda lime shows that the filtrate from the mercuric iodide sample is practically free from albumen, it is evident that the numbers obtained in this way must be a near approximation to the truth.

The Process of Analysis.

The reagents, apparatus and manipulation necessary to give the most reliable results in milk sugar estimation are as follows:

Reagents.—1. *Basic plumbic acetate*, sp. gr. 1.97. Boil a saturated solution of sugar of lead with an excess of litharge, and make it of the strength indicated above. One cubic centimetre of this will precipitate the albumens in 50 to 60 cc. of milk.

2. *Acid mercuric nitrate* dissolves mercury in double its weight of nitric acid, sp. gr. 1.42. Add to the solution an equal volume of water. One cubic centimetre of this reagent is sufficient for the quantity of milk mentioned above. Larger quantities can be used without affecting the results of polarisation.

3. *Mercuric iodide with acetic acid* (composition already given).

Apparatus.

1. Pipettes marked at 59.5, 60 and 60.5 cc.
2. Sugar flasks marked at 102.4 cc.
3. Filters, observation tubes and polariscope.
4. Sp. gr. spindle and cylinder.
5. Thermometers.

Manipulation.

1. The room and milk should be kept at a constant temperature. It is not important that the temperature should be any given degree. The work can be carried on equally well at 15°, 20° or 25°. The slight variations in rotatory power within the above limits will not affect the result for analytical purposes. The temperature selected should be the one which is most easily kept constant.

2. The sp. gr, of milk is determined. For general work this is done by a delicate sp. gr. spindle. Where greater accuracy is required use sp. gr. flask.

3. If the sp. gr. be 1.026 or nearly so, measure out 60.5 cc. into the sugar flask. Add 1 cc. of mercuric nitrate solution or 30 cc. mercuric iodide solution and fill to 102.4 cc. mark. The precipitated albumen occupies a volume of about 2.4 cc. Hence the solution is really 100 cc. If the sp. gr. is 1.030 use 60 cc. of milk. If sp. gr. is 1.034 use 59.5 cc. milk.

4. Fill up to mark in 102.4 cc. flask, shake well, filter and polarise.

Notes.

In the above method of analysis the specific rotatory power of milk sugar is taken at 52.5, and the weight of it in 100 cc. solution to read 100 degrees in the cane sugar scale at 20.56 grams. This is for instruments requiring 16.19 grams sucrose to produce a rotation of 100 sugar degrees. It will be easy to calculate the number for milk sugar whatever instrument is employed.

Since the quantity of milk taken is three times 20.56 grams, the polariscopic readings divided by 3 give at once the percentage of milk sugar when a 200 mm. tube is used.

If a 400 mm. tube is employed, divide reading by 6; if a 500 mm. tube is used, divide by 7.5.

Since it requires but little more time, it is advisable to make the analysis in duplicate, and take four readings for each tube. By following this method gross errors of observation are detected and avoided.

By using a flask graduated at 102.4 for 60 cc. no correction for volume of precipitated caseine need be made. In no case is it necessary to heat the sample before polarising.

THE CHEMICAL COMPOSITION OF WHEAT AND CORN AS INFLUENCED BY ENVIRONMENT.

By Clifford Richardson.

During the past two years an examination of a large number of American wheats and corns has been completed in the laboratory of the United States Department of Agriculture.

The specimens, collected from all parts of the country and grown under the most varied conditions, have afforded an opportunity for the study of the effects of soil, climate and methods of cultivation upon the chemical composition and physical condition of the two cereals.

It is my intention here to give a *résumé* of the principal results of the work, referring for details to the original reports, which can be had by application to the Department of Agriculture at Washington.

Wheat.

Four hundred and seven analyses of wheat are included in our tables, and from them the averages have been drawn for the composition and weight per hundred grains of the wheats of the whole country, of different sections and for particular States, which are given in the tables below.

In two hundred and sixty of the samples the oil and fibre were determined, and from these analyses, made in 1882, averages, including these constituents and the carbhydrates, have been calculated.

From the preceding analyses the following facts are derived. American wheats are deficient in albuminoids as compared with those of foreign countries. They are, too, lighter in weight per hundred grains; they contain less water, about the same percentage of ash, more oil, and a smaller amount of fibre. For comparison the averages for foreign grain are given.

The smaller amount of water in our wheats is due, undoubtedly, to a drier climate. The question of hygroscopicity will, however, be considered in another paper.

The average amount of ash differs very little in wheats from our own and from foreign countries, but among the individual analyses many specimens of grain grown on new and rich soil will be found which have an increased amount of this constituent.

In oil our wheats are much richer, but the question arises whether the more complete methods of extraction of the present day make the results entirely comparable.

The amount of fibre is decidedly smaller, as was found to be the case in American grasses. This, in both cases, is due to our hotter summers and shorter period of growth.

AVERAGE COMPOSITION OF AMERICAN WHEATS.

Locality.	Number of analyses.	Number of weights.	Weight of 100 grains.	Water.	Ash.	Undetermined.*	Albuminoids.	Nitrogen	Weight of 100 grains.		Albuminoids.	
									Highest.	Lowest.	Highest.	Lowest.
			Grams.	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Grams.	Grams.	Per Cent	Per Cent
U. S. and British America	407	377	3.644	10.16	1.92	75.77	12.15	1.94	5.924	1.830	18.03	7.70
Atlantic and Gulf States	117	105	3.489	10.34	1.77	76.54	11.35	1.81	5.079	1.830	15.58	9.43
Middle States	91	89	3.537	10.61	1.85	75.04	12.50	2.00	5.800	2.138	16.63	10.15
Western States	177	166	3.763	9.83	2.06	75.37	12.74	2.04	5.924	2.561	18.03	8.93
Pacific States	20	15	4.901	10.25	1.87	78.15	9.73	1.56	5.745	2.584	12.78	7.70
Canada	6	...	3.325	9.74	1.56	77.83	10.87	1.74	3.686	2.964	14.70	9.45
Pennsylvania	33	26	3.373	10.73	1.70	76.13	11.44	1.83	4.658	2.035	15.58	9.45
Maryland	9	...	3.597	10.52	1.75	76.08	11.65	1.86	5.079	3.075	14.53	9.80
Virginia	15	14	3.433	9.98	1.84	76.08	12.10	1.93	4.283	1.830	14.00	10.15
West Virginia	2	1	3.392	8.55	2.07	78.44	10.94	1.75	.....	.....	11.03	10.85
North Carolina	22	...	3.776	10.03	1.59	77.95	10.43	1.67	4.628	2.780	12.43	8.93
Georgia	7	...	3.579	10.00	1.96	76.26	11.78	1.89	4.627	2.834	14.00	9.45
Alabama	19	19	3.424	10.82	1.96	75.93	11.29	1.80	4.647	2.011	13.65	9.80
Ohio	44	44	3.476	10.68	1.94	74.55	12.83	2.05	5.800	2.663	16.10	10.68
Tennessee	15	14	3.150	10.24	1.92	75.34	12.50	2.00	3.990	2.138	16.63	10.15
Kentucky	8	..	3.454	10.83	1.75	74.27	13.15	2.10	3.666	3.146	14.53	11.90
Michigan	22	...	3.969	10.71	1.64	75.98	11.67	1.87	4.902	3.402	15.23	10.50
Missouri	12	...	3.502	9.80	1.92	76.72	11.56	1.86	3.867	3.098	14.00	10.50
Arkansas	1	...	.....	9.56	2.52	74.97	12.95	2.07	.....	.....	.....	.....
Minnesota	13	13	3.245	9.96	1.77	75.08	13.19	2.11	3.867	2.720	17.15	10.85
Dakota	12	12	3.149	8.84	1.96	74.25	14.95	2.40	3.700	2.771	18.03	12.43
Manitoba	2	2	3.288	8.35	1.63	75.49	14.53	2.32	.....	.....	.....	.....
Kansas	10	...	3.204	11.80	1.64	75.41	11.15	1.78	3.424	2.881	12.25	10.50
Texas	19	...	2.847	10.03	1.81	75.02	13.14	2.10	3.937	2.561	15.23	10.68
Colorado	106	98	4.214	9.73	2.21	75.33	12.73	2.03	5.924	2.716	15.94	8.93
Utah	2	2	3.893	9.17	2.23	78.45	10.15	1.62	4.084	3.703	10.50	9.80
New Mexico	2	2	3.572	9.30	1.98	78.22	10.50	1.68	3.956	3.188	11.73	9.28
California	10	10	3.892	10.73	1.86	76.47	10.94	1.75	5.184	3.095	12.78	9.10
Oregon	8	...	5.044	9.74	1.84	79.82	8.60	1.37	5.745	4.253	9.47	8.05
Washington Territory	2	2	3.655	9.89	1.98	79.90	8.23	1.32	4.726	2.584	8.75	7.70

* Fibre, carbhydrates and fat.

AVERAGE COMPOSITION OF AMERICAN WHEATS.

No. of analyses.	Locality.	Weight of 100 grains.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.	Heaviest 100 grains.	Lightest 100 grains.	Highest albuminoids.	Lowest albuminoids.
		Grams.	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Grams.	Grams.	Per Cent	Per Cent
260	United States and Canada..	3.638	10.27	1.84	2.16	71.98	1.80	11.95	1.91	5.924	1.830	17.15	8.05
108	Atlantic and Gulf States...	3.464	10.42	1.75	2.17	72.61	1.72	11.33	1.81	5.079	1.830	15.58	9.45
47	The Middle West.....	3.607	10.51	1.76	2.01	71.67	1.90	12.15	1.94	4.902	2.138	16.63	10.15
97	West of the Mississippi....	3.806	10.04	1.99	2.22	71.12	1.87	12.76	2.04	5.924	2.561	17.15	10.15
8	The Pacific coast.....	5.044	9.74	1.84	2.08	76.18	1.56	8.60	1.37	(5.745)	(4.253)	9.47	8.05
6	Canada	3.325	9.74	1.56	2.29	73.87	1.67	10.87	1.74	3.686	2.964	14.70	9.45
32	Pennsylvania	3.373	10.72	1.67	2.05	72.45	1.73	11.38	1.82	4.658	2.035	15.58	9.45
9	Maryland	3.597	10.52	1.75	2.09	72.25	1.74	11.65	1.86	5.079	3.075	14.53	9.80
11	Virginia	3.343	10.34	1.70	2.21	71.87	1.71	12.71	1.95	4.208	1.830	14.00	10.15
7	Georgia.....	3.579	10.00	1.96	2.30	72.24	1.72	11.78	1.89	4.627	2.834	14.00	9.45
22	North Carolina.	3.776	10.03	1.59	2.25	73.94	1.76	10.43	1.67	4.628	2.780	12.43	8.93
17	Alabama.....	3.314	10.94	2.03	2.21	71.84	1.62	11.36	1.79	4.047	2.011	13.65	9.80
	Michigan (Kedzie).....	.....	11.28	1.73	.....	74.97	.....	12.02	1.92	.....	.....	13.78	9.13
22	Michigan.....	3.969	10.71	1.64	2.06	72.12	1.80	11.67	1.87	4.902	3.402	15.23	10.50
8	Kentucky	3.454	10.83	1.75	1.87	70.37	2.03	13.15	2.10	3.666	3.146	14.53	11.90
14	Tennessee	3.150	10.19	1.89	2.00	71.33	2.02	12.51	2.00	3.990	2.138	16.63	10.15
12	Missouri.....	3.502	9.80	1.92	2.19	72.36	2.17	11.56	1.86	3.867	3.098	14.00	10.50
9	Minnesota.....	3.354	10.60	1.71	2.03	70.96	2.04	12.66	2.03	3.828	3.116	17.15	10.85
10	Kansas	3.204	11.80	1.64	1.98	71.35	2.08	11.15	1.78	3.424	2.881	12.25	10.50
19	Texas	2.847	10.03	1.81	2.11	70.85	2.06	13.14	2.10	3.937	2.561	15.23	10.68
45	Colorado.....	4.682	9.57	2.21	2.38	70.91	1.62	13.31	2.13	5.924	3.851	15.94	11.19
8	Oregon.....	5.044	9.74	1.84	2.08	76.18	1.56	8.60	1.37	5.745	4.253	9.47	8.05

AVERAGE COMPOSITION OF FOREIGN WHEATS.

Locality.	Authority.	No. of analyses.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Highest albuminoids.	Lowest albuminoids.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Russian	Laskowsky	24	11.49	.....	1.57	.....	.....	19.48	24.56	10.68
German	Wolff	....	14.40	1.70	1.50	66.40	3.00	13.00	.....	.....
Continental	Peligot	14	14.00	1.60	1.20	66.90	1.70	14.60	21.50	10.60
do.	Millon	16	13.82	1.57	1.74	70.13	1.70	11.04	13.81	9.92
do.	Reiset	20	14.43	1.99	.....	70.58	.....	13.00	17.94	10.69
World	König	200	13.56	1.79	1.70	67.87	2.66	12.42	24.16	8.19
do.	Kühn	.....	14.30	1.70	1.60	66.20	3.00	13.20	24.10	8.20

Maxima and minima of albuminoids, percentage of nitrogen, and weight of 100 grains of wheat.

No. of analyses.	Locality.	Authority.	Per cent. of nitrogen.	Per cent. of albuminoids.	Albuminoids.		Weight of 100 grains.		
					Maximum.	Minimum.	Average.	Maximum.	Minimum.
					Pr cent.	Pr cent.	Grams.	Grams.	Grams.
25	North German	Von Bibra	2.20	13.76	18.25	9.80	4.270	7.450	3.200
20	South German	do.	2.13	13.28	17.81	9.68	4.473	7.000	2.870
14	Scotch	do.	2.07	12.95	14.63	11.06	4.679	5.200	3.855
5	Egypt	do.	1.46	9.10	9.94	8.75	.....	.....	.....
2	Australian	do.	1.60	9.98	9.98	9.94	.....	.....	.....
13	Algerian	do.	2.20	13.75	15.50	11.25	5.540	6.525	4.600
9	Spanish	do.	2.30	14.35	24.13	11.25	4.278	5.125	3.850
7	Russian	do.	2.45	15.31	21.70	11.44	3.950	5.350	1.800
24	do.	Laskowsky	3.13	19.48	24.16	10.68	.....	.....	.....
.....	England	Lawes and Gilbert	2.20	13.76	15.50	11.25	.....	.....	.....
.....	Germany	Mayer	2.20	13.75	.....	.....	.....	.....	.....
.....	do.	Wolff	2.08	13.00	.....	.....	.....	.....	.....
15	Continental	Millon	1.88	11.75	12.63	9.88	.....	.....	.....
12	do.	Peligot	2.23	13.97	21.50	9.90	.....	.....	.....
20	do.	Reiset	2.04	12.78	17.90	10.68	.....	.....	.....
176	Average, excluding Russia	König	1.98	12.35	21.37	7.61	.....	.....	.....
.....	Average of world	Kühn	2.11	13.20	24.10	8.20	.....	.....	.....

The average percentage of albuminoids is, for the whole country, lower than for most foreign grain, as has been said, and in no individual case even reaches the amount found in Russian wheat. Whilst among ours the highest percentage occurs in a spring wheat from Dakota, 18.03 per cent., Laskowsky found in a Russian wheat as much as 24.56 per cent., and in twenty-four specimens an average of 19.48 per cent. That the lack of albuminoids in American wheats is not due entirely to enhanced formation of starch is shown by the fact that the weight of one hundred grains of American wheat is no greater, in fact somewhat smaller, than that of foreign specimens.

The variations in the composition of wheat, as well as in the weight per hundred grains, are large. Among our analyses the following extremes are found:

Limits of Variation in the Percentages of the Constituents of Wheats and in Weight per Hundred Grains.

	Highest per cent.	Lowest per cent.	Variation.	Above aver.	Below aver.
Water, . .	12.49	7.67	4.82	2.33	2.49
Ash, . . .	3.57	.80	2.77	1.65	1.12
Oil, . . .	3.57	1.40	2.53	1.77	.76
Carbhydrates, .	78.66	64.84	13.82	6.68	7.14
Fibre, . .	3.05	.44	2.61	1.25	1.36
Albuminoids, .	18.03	7.70	10.33	5.88	4.45
Weight of 100 grains,	5.924	1.830	4.094	2.286	1.808

These extremes are in no case due to accidental errors of analyses, as all determinations on which the table is based have been made in duplicate.

The striking feature of the table is that among the important constituents the variation in the albuminoids is the greatest, and the liability to variation in this constituent is a peculiarity of the wheat grain strongly in contrast with maize, as will be seen hereafter. It will be noticed also that the lowest percentages are not as far below as the highest percentages are above the average.

How far these variations are due to the different conditions under which the wheats were grown can be more easily determined by examining the averages for the different sections of the country, which will be seen to depart somewhat from the general average.

The eastern wheat is poorest in ash, albuminoids and size of the

grain. A regular gradation of improvement in this respect takes place from east to west. On the Pacific Coast, however, especially in Oregon, although the size of the grain is very nearly the largest in the country, the albuminoids are the lowest. The question arises how much is due to climate and how much to soil and variety. As regards variety, spring wheats contain much more albuminoid matter than winter grain. They are richer in nitrogen because they have a short period of vegetation and do not, therefore, have an opportunity to store up as much starch. The winter wheats, on the contrary, producing more starch, have a relatively lower percentage of nitrogen but greater weight.

The effect of climate may be very similar; a hot and dry season, of course, shortening the period of growth and hastening the time of ripening. The amount of starch stored in the grain is thus reduced, and the relative percentage of albuminoids increased. This is well illustrated by two wheats from Dakota, one a winter, the other a spring variety, having the following weights per hundred grains and percentages of albuminoids:

	Weight of 100 grains.	Per cent. of albuminoids.
Winter,	3.513	10.68
Spring,	2.755	14.35

If the former were diminished in size and weight, at the expense of its store of starch, it would approach the latter in its relative percentage of albuminoids.

In examining the averages for differences due to climatic causes affecting the accumulation of starch, it is evident that, as our summers are hot and the period of growth consequently short, the albuminoids in American wheat, as a whole, should be higher than that grown in cooler Continental climates. The effect of our hotter and shorter season of ripening does in fact diminish the amount of fibre, and even the size of the grain, but not sufficiently to produce any relative increase in the albuminoids.

In certain parts of the country it has been found that a moist or cool climate has the effect of producing a largely increased formation of starch, and consequent reduction in relative amount of albuminoids and increase in the weight of the grain. I refer to Oregon.

In other local instances the climate has, in conjunction with other conditions of environment, produced a large grain, but the soil and irrigation have been able to furnish supplies of nitrogen sufficient to keep up the relative percentage of albuminoids, or even to raise it above the average. This is the case with Colorado, which will shortly be considered.

As a whole, however, the increase in albuminoids from east to west, followed by an increased weight, denotes that climatic influences are not paramount, and that the changes are due to the soil; the more exhausted soils of the east not being able to furnish such supplies of nitrogenous and ash constituents as the richer ones of the west, the gradual change in composition corresponding to the relative exhaustion of the farming lands.

In Colorado the effect of favorable surroundings, both as regards soil and climate, in producing a fine wheat is well illustrated. The specimens which have been examined were grown on the farm of the Colorado Agricultural College at Fort Collins, by Prof. A. E. Blount. Every care has been taken, both in the selection of the seed, by crossing varieties and by careful cultivation and irrigation, on a new soil particularly adapted to wheat, to obtain a perfect grain. The result has been that the wheats are distinguished by a high percentage of albuminoids, combined with a large weight per hundred grains, thus realising what is most desirable. The albuminoids are not as high as in many spring wheats of the northwest, but their greater size make them of more value by increasing the proportion of flour to bran.

The results have thus far been realised only on an experimental scale, but they serve as well to illustrate the susceptibility of the grain to its surroundings and the possibilities for its improvement.

The analyses extend over three succesive years, and the average for each season is given in the following table :

AVERAGE COMPOSITION OF COLORADO WHEAT, CROPS OF 1881, 1882 AND 1883.

	1881.	1882.	1883.
Number of varieties analysed	33	12	57
Weight of 100 grains.....grams	4.865	4.283	3.941
Water.....per cent.	9.86	8.80	9.38
Ash.....do	2.28	1.99	2.09
Oil.....do	2.41	2.38	76.79
Carbhydrates.....do	70.48	72.08	
Crude fibre.....do	1.57	1.76	
Albuminoids.....do	13.40	13.04	11.74
	100.00	100.00	100.00
Nitrogen.....do	2.14	2.09	1.88

It will be noticed that the crop of 1883 is not equal to those of preceding years, either in weight of the grain or in albuminoids. This is explained by the fact that in June, 1883, when the wheats were in the formation stage, there was a heavy and destructive hail-storm which severely injured the plants. This, occurring at a time when the grain was storing up its albumen, injured it seriously in this respect especially; while the recovery of the plant later resulted in almost the usual increase due to starch and a vigorous growth, encouraged by the moist season which followed. This seems to be sufficient reason for the deficient quality of the crop of 1883.

How differently similar conditions, occurring at other periods of growth, may affect the grain is illustrated by wheat from Ohio grown the same year. These were injured by severe rains just before ripening. The resulting crop was not plump in consequence, and therefore of light weight, owing to its lack of opportunity to fill out the grain with starch. The percentage of albuminoids was, therefore, relatively high, and were the condition of growth unknown, and the size and appearance of the grain unobserved, a mere chemical analysis would be very misleading.

In addition to the generally high average composition of Colorado wheat, as shown by the averages of favorable seasons, we learn much from the study of the individual varieties.

The improvement in seed sent from other localities is marked even in the first crop. For instance, even in the unfavorable season of 1883, eight seed wheats, distributed by the Department of Agriculture, furnished crops which showed a marked improvement, as may be seen by the following comparison:

COMPARISON OF DEPARTMENT SEED AND COLORADO CROPS, 1882-83.

Serial number.	Weight of 100 grains.		Water.		Ash.		Albuminoids.		Nitrogen.	
	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.	Seed.	Crops.
	Grams.	Grams.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
2173.....	4.152	...	9.84	...	1.73	...	9.98	...	1.60	...
2174.....	...	4.182	...	9.69	...	2.19	...	11.20	...	1.79
2175.....	3.650	...	9.40	...	1.94	...	11.73	...	1.88	...
2176.....	...	3.650	...	9.50	...	2.10	...	13.65	...	2.18
2177.....	2.820	...	9.74	...	1.94	...	12.60	...	2.02	...
2178.....	...	4.594	...	9.55	...	1.95	...	12.95	...	2.07
2179.....	4.336	...	9.90	...	1.86	...	10.33	...	1.65	...
2180.....	...	4.957	...	10.25	...	2.10	...	12.43	...	1.99
2181.....	2.612	...	11.35	...	1.75	...	12.60	...	2.02	...
2182.....	...	3.231	...	11.11	...	2.04	...	12.60	...	2.02
2183.....	4.084	...	10.50	...	1.95	...	9.80	...	1.57	...
2184.....	...	3.818	...	9.44	...	2.17	...	11.38	...	1.82
2185.....	3.062	...	10.38	...	1.89	...	10.15	...	1.62	...
2186.....	...	2.879	...	9.21	...	2.04	...	10.33	...	1.65
2187.....	3.138	...	9.48	...	2.56	...	16.45	...	2.63	...
2188.....	...	4.064	...	9.92	...	2.20	...	14.53	...	2.32
Average.	3.482	3.922	10.07	9.83	1.95	2.10	11.71	12.38	1.88	1.98
Gain.....	...	6	...	3	...	7	...	7	...	7
Loss.....	...	2	...	5	...	1	...	1	...	1

The crop, as a whole, has improved in ash and albuminoids, and in the size of the grain; while taken individually, there has been a loss in size only twice, and ash and albuminoids in but one variety. Why this has occurred will appear later on.

In the crops of 1881 and 1882 we find the conditions such that the yield after three years' growth has been increased, in some varieties on which observations have been made, to a marvellous extent.

YIELD FROM ONE GRAIN OF DIFFERENT VARIETIES OF WHEAT INTRODUCED INTO COLORADO.

Variety.	Yield first year.	Yield second year.	Yield third year.
Black Bearded Centennial	...	...	203
Judkin	...	...	320
Australian Club	...	...	416
White Fountain	440	...	...
Russian	76	172	448
Touzelle	56	128	480
German Fife	112	...	...
Oregon Club	...	...	480
Sonora	56	110	448
Improved Fife	56	126	416
Lost Nation	76	96	352
Clawson	68	136	544

Selection of the seed, climate, soil, cultivation and irrigation have done this.

Studying the chemical composition and weight of certain varieties in the favorable season of 1882, some interesting facts are discovered.

Twelve selected seed wheats, many of them of very high quality, were sent to the Colorado farm by the Department of Agriculture and the crops returned for analysis. A comparison of the two series is here given.

COMPARISON OF DEPARTMENT SEED AND COLORADO CROP.

Variety.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Weight of 100 grains.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Grams.
McGehee's Red :							
Department.	10.00	1.04	2.46	71.57	1.46	13.47	2.811
Colorado.....	10.00	1.80	1.92	70.85	1.76	13.67	4.159
Finlay :							
Department.	10.00	1.59	2.37	73.22	1.17	11.65	3.285
Colorado.....	10.00	1.83	2.34	71.60	1.72	12.51	4.125
Champ. Amber :							
Department.	10.00	1.88	2.19	73.70	1.33	10.90	3.278
Colorado.....	10.00	2.16	2.42	72.24	1.52	11.66	4.347
Dallas :							
Department.	10.00	2.10	2.43	71.54	1.61	12.32	4.023
Colorado.....	10.00	1.85	2.46	69.34	1.73	14.52	4.610
Bennett :							
Department.	10.00	2.01	2.17	70.77	1.35	13.70	3.218
Colorado.....	10.00	2.15	2.52	70.00	2.00	13.33	3.976
Lemon :							
Department.	10.00	1.87	2.46	68.87	1.50	15.30	3.417
Colorado.....	10.00	2.02	2.10	72.01	1.65	12.22	4.335
Gold Medal :							
Department.	10.00	1.77	2.33	74.89	1.36	9.65	3.076
Colorado.....	10.00	1.78	2.24	72.11	1.72	12.15	4.374
German Amber :							
Department.	10.00	1.66	2.57	74.01	1.02	10.74	2.938
Colorado.....	10.00	1.77	2.39	71.84	1.73	12.27	4.027
Rice :							
Department.	10.00	2.11	2.28	69.73	1.60	14.28	3.586
Colorado.....	10.00	2.06	2.35	69.70	1.94	13.95	4.103
Wash'ton Glass :							
Department.	10.00	2.02	2.19	72.20	1.81	11.88	3.741
Colorado.....	10.00	1.92	2.37	73.16	1.16	11.39	4.450
Swamp :							
Department.	10.00	2.04	2.01	68.05	1.79	16.11	3.660
Colorado.....	10.00	2.05	2.30	68.89	1.85	14.91	4.423
Wysor :							
Department.	10.00	1.54	2.14	72.11	1.72	12.49	3.796
Colorado.....	10.00	2.22	2.16	71.13	2.09	12.40	4.609
Average Seed :							
Department.	10.00	1.80	2.30	71.72	1.47	12.75	3.402
Colorado.....	10.00	1.97	2.30	71.07	1.74	12.92	4.299
Gain for crop.....	.....	9	7	9	11	6	12
Loss..	.....	3	5	3	1	6	0

The average composition of the seed wheats is, to begin with, as has been said, good, and many of them are high in albuminoids. The weights of one hundred grains are, however, rather low. The average for the crop shows a slight gain in ash, no change in oil, a gain in fibre and a small rise in albuminoids.

The gain in ash is due to richer soil, that in fibre to the longer vegetative period; but the question arises why there has not been a greater gain in albuminoids? This can be explained by a study of the individual analyses. It has been shown that the average amount of albuminoids in the whole crop of 1882 was about 13 per cent., and it will be seen that those that were from seed containing higher percentages than this fell toward it, while those lower in amount rose; that is to say, six increased and six diminished in the amount of albuminoids they contained. This seems to point to the fact that in the season of 1882 the conditions were such that the soil of Colorado was able to produce a wheat containing about thirteen per cent. of albuminoids, and that if the seed sown contained more than this, there was a tendency toward a decrease in amount, and the reverse. Reversion, apparently, takes place more easily than improvement.

In considering this point, regard must be had for the fact that, while the relative amounts of albuminoids average the same in both seed and crop, they are not absolutely the same, because there has been a large increase in the size of the grain, in fact over twenty-five per cent. There must have been, consequently, an absolute increase of the same amount of nitrogenous substance in order to preserve the same ratio.

That the quality of the seed has an effect on the crops is made apparent by a division of the analyses of the crops of 1882 into certain classes, as has been done in the next table, according to the source of the seed.

Colorado Crops of 1882.

	33 Varieties.	Averages of		
	All.	Russian.	Foreign.	Domestic.
Weight of 100 grains,	4.865	5.075	5.187	4.714
Water,	9 86	9.69	9.86	9.85
Ash,	2.28	2.41	2.32	2.27
Oil,	2.41	2.44	2.45	2.38
Carbhydrates,	70.48	69.49	69.46	70.87
Crude fibre,	1.57	1.59	1.57	1.58
Albuminoids,	13.40	14.54	14.34	13.05

The Russian seeds were of the best quality, and the crops correspond. The domestic seeds were of poor quality, and the crops correspondingly low.

The conditions in Colorado do not seem to permit the production, for any length of time, of a grain containing, as the Russian varieties do, more than 13 per cent. Reversion begins at once in grains having a higher amount. Nos. 2187 and 2188, analyses of which are given in a preceding table, illustrate this, 2187 being a Russian spring wheat with 16.45 per cent. of albuminoids, and the crop from it, 2188, having 14.53 per cent. Another year 2188 would probably fall still lower, but not quite as low as the usual average of 13 per cent.

Analyses of the grain of 1884 have not yet been made, but they will undoubtedly furnish some results of interest.

In concluding the subject of wheat, attention must be called to the recent experiments, published in the Journal of the Chemical Society,[1] by Lawes and Gilbert. Their results, derived from the analyses of 92 specimens of wheat grain and wheat straw, in which the ash constituents and nitrogen were determined, and which were grown under the most varied conditions of soil and season, agree in many respects with our conclusions derived from Ohio, Minnesota, Dakota, Colorado and Oregon grain.

Maize.

Analyses of maize, about two hundred in number, have furnished the basis for the following averages:

AVERAGE COMPOSITION OF AMERICAN CORN.

Locality.	Ash.	Albuminoids.	Nitrogen.	Number of analyses.	Lowest albuminoids.	Highest albuminoids.
	Per cent.	Per cent.	Per cent.		Per cent.	Per cent.
America, 1882	1.52	10.46	1.67	114	7.00	13.05
America, 1883	1.58	10.31	1.65	88	7.88	12.63
Average	1.55	10.39	1.66	202	7.00	13.65
New York	1.43	10.54	1.69	9	9.10	12.43
Illinois	1.48	10.06	1.61	20	7.88	12.08
Minnesota	1.68	10.07	1.61	16	8.40	12.43
Dakota	1.57	10.75	1.72	15	9.28	12.25
Nebraska	1.54	10.47	1.68	13	9.10	12.25
Colorado	2.23	9.89	1.58	4	8.93	12.25
California	1.56	10.26	1.64	11	8.40	11.73

[1] Jour. Chem. Soc. 1884, 45, August.

AVERAGE COMPOSITION OF AMERICAN CORN (MAIZE).

Locality.	Weight of 100 kernels.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.	Weight of largest 100 kernels.	Weight of smallest 100 kernels.	Highest albuminoids.	Lowest albuminoids.	No. of analyses.	No. of weights of 100 kernels.	Analyst.
	Grams.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Pr. ct.	Grams.	Grams.	Pr. ct.	Pr. ct.			
America	36.910	10.04	1.52	5.20	70.69	2.09	10.46	1.67	52.679	23.605	13.65	7.00	114	61	
Northern States.	37.320	9.98	1.54	5.11	71.32	1.41	10.64	1.70	44.147	30.610	13.65	7.53	30	3	
South	.....	8.96	1.37	4.94	72.06	1.72	10.95	1.75	.....	.....	11.03	10.88	2	..	
Middle West	32.457	12.33	1.43	4.97	68.16	2.22	10.89	1.70	.....	.....	12.00	9.29	15	1	
Far West	37.528	9.50	1.55	5.30	70.75	2.47	10.43	1.67	52.679	28.348	12.78	8.23	53	53	
Pacific Slope	27.900	9.78	1.48	6.40	72.13	2.07	8.14	1.30	.....	.....	8.40	7.88	2	1	
Mexico	.....	9.58	1.58	5.48	71.34	1.68	10.34	1.65	.....	.....	10.67	10.15	3	...	
New Hampshire	.....	10.10	1.58	5.48	70.15	1.11	11.67	1.85	.....	.....	13.65	10.50	11	...	Department of Agriculture.
Vermont	.....	8.64	1.45	5.63	72.76	1.38	10.14	1.62	.....	.....	.....	.....	1	...	do.
Connecticut	.....	10.84	1.54	4.70	70.98	1.46	10.48	1.69	.....	.....	11.63	9.19	13	...	S. W. Johnson, W. O. Atwater.
Pennsylvania	37.320	7.96	1.43	5.22	74.54	1.97	8.88	1.42	44.147	30.610	10.15	7.53	5	3	Department of Agriculture.
North Carolina	.....	8.96	1.37	4.94	72.06	1.72	10.95	1.75	.....	.....	11.03	10.88	2	...	Johnson and Department.
Kentucky	32.457	7.70	1.50	5.33	73.47	2.20	9.80	1.57	.....	.....	.....	.....	1	...	Department of Agriculture.
Tennessee	.....	7.58	1.23	5.09	74.16	2.65	9.29	1.48	.....	.....	.....	.....	1	...	do.
Indiana	.....	11.29	1.28	4.87	70.16	1.90	10.50	1.68	.....	.....	.....	.....	1	...	R. C. Kedzie.
Michigan	.....	13.20	1.45	4.95	67.05	2.21	11.14	1.73	.....	.....	12.00	9.88	12	...	do.
Missouri	38.411	8.18	1.68	5.28	72.00	2.33	10.54	1.68	52.679	30 674	12.78	8.23	26	26	Department of Agriculture.
Kansas	33.271	11.94	1.49	4.87	69.39	2.16	10.15	1.62	36.687	28.348	10.68	9.10	6	6	do.
Colorado	34.120	10.50	1.50	5.66	70.19	2.35	9.80	1.60	.....	.....	.....	.....	1	1	do.
Texas	37.833	10.44	1.42	5.45	69.52	2.77	10.40	1.66	43.799	30.898	11.03	9.80	20	20	do.
Oregon	....	9.25	1.46	7.08	73.07	1.26	7.88	1.26	.....	.....	.....	.....	1	...	do.
Wash. Territory.	27.900	10.30	1.50	5.73	71.19	2.88	8.40	1.34	.....	.....	.....	.....	1	...	do.
Mexico	.....	9.58	1.58	5.48	71.34	1.68	10.34	1.65	.....	.....	10.67	10.15	3	...	do.

A part of these, 114 in number, have been examined in greater detail, and from them other averages have been deduced.

In comparison with the averages of other investigators on the Continent, there will be seen to be a much greater degree of agreement than was the case with wheat.

AVERAGE OF AMERICAN CORN COMPARED WITH AVERAGES OF FOREIGN INVESTIGATIONS.

Constituent.	Richardson.	Koenig.	Wolff.
Water	10.04	13.12	14.40
Ash	1.52	1.51	1.50
Oil	5.20	4.62	6.50
Carbhydrates	70.69	68.41	62.10
Fibre	2.09	2.49	5.50
Albuminoids	10.46	9.85	10.00
	100.00	100.00	100.00
Nitrogen	1.67	1.58	1.60
Number of analyses	114	145	...

A study of the extremes in the percentages of the various constituents given in the next table shows that the variations are within smaller limits in maize than in wheat, at least for most of them.

VARIATIONS OR EXTREMES FOR EACH CONSTITUENT OF CORN.

Constituent.	Highest percentage.	Lowest percentage.	Variation.	Above average.	Below average.
Water	15.10	7.40	7.70	5.06	3.64
Ash	3.08	1.03	2.05	1.53	.55
Oil	7.49	3.92	3.57	2.29	1.28
Carbhydrates	75.73	65.97	9.76	5.04	4.72
Fibre	3.10	.78	2.32	1.01	1.31
Albuminoids	13.65	7.00	6.65	3.19	3.46
Weight of 100 kernels, grams	53.679	23.605	29.074	15.769	13.305

The variations are somewhat larger in moisture in maize, but the albuminoids never reach the high percentages at times found in wheat. Maize is influenced by the same causes as wheat, but its longer vegetative period renders it more independent of its environment, at least as far as the composition of the grain is concerned. The averages for different parts of the country are more nearly alike. In some cases, where the analyses are few in number, the averages are low, but excluding these, since they are hardly representative, the remainder vary but slightly. The few specimens

from the Pacific Coast, like the wheats from that locality, are poor in albuminoids. This may be due to the same climatic causes, but the average weight per hundred kernels is not above that of the rest of the country, and, therefore, the poverty in nitrogen can hardly be attributed to enhanced starch formation. The size of the kernel of maize, in fact, does not seem to influence its composition as it does in the case of wheat. In the original report upon this subject the weights of a thousand specimens from all parts of the country show the extremes of size to be very wide apart, viz. 64.102 and 13.858 grams per hundred, and yet the following analyses of certain specimens, selected at each extreme, show that, while the largest kernels seem to have made their increase in size somewhat at the expense of the albuminoids, and the smallest to be slightly richer in nitrogen from lack of starch in the kernel, the difference between the two kinds, large and small, is not as great as might be expected from our previous experience with wheat, for in each group we find a grain having the same percentage of albuminoids, 9.45. The longer vegetative period and the stronger roots must be the explanation of these facts in regard to maize.

ANALYSES OF THE LARGEST AND SMALLEST KERNELS OF MAIZE SELECTED FROM 1000 SPECIMENS.

	Weight of 100 kernels.	Albuminoids.
	61.141	8.58
	64.102	9.63
	63.384	9.45
	60.909	8.58
Average, largest,	62.359	9.09
	18.698	11.90
	22.091	9.45
	19.982	10.33
	16.073	10.33
Average, smallest,	19.211	10.50

It is my intention to extend this investigation to the other cereals, oats, barley and rye, and to continue the collection of data in regard to wheat and maize. In conclusion, I desire to call attention to a typographical error in the table on page 29 of Bulletin No. 4. The average albuminoids for the United States and Provinces should read 12.53 instead of 10.53.

Contributions from the Sheffield Laboratory of Yale College.

XXI.—ON THE RELATIVE DIGESTIBILITY OF FISH FLESH IN GASTRIC JUICE.

By R. H. Chittenden and Geo. W. Cummins.

The value of food as nutriment depends primarily upon the presence in suitable quantity of elements, or combination of elements, capable of supplying the needs of the body; coupled with this, however, is the ease with which the food stuff in question can be rendered available by the system for its wants. This, or in other words its *digestibility*, constitutes a very important item in determining the true nutritive value of any food. If, of two foods possessing a like chemical composition, one be more easily digestible, that one, though containing no more available nutriment than the other, is in virtue of its easier digestibility more valuable as a food stuff and in one sense more nutritious, as well as more economical for the system.

Both chemists and physiologists have appreciated the importance of all data relative to the nutritive value of foods. But hitherto nearly all work in this direction has been confined to a study of chemical composition, and only occasionally to digestibility. The mere fact, however, that a substance contains a certain percentage of nitrogen is not alone sufficient. We need to know in addition, not only how much of the nitrogen passes through the body unabsorbed, thus indicating how much is ordinarily available for nutriment, but we need to know likewise how long the food stuff remains in the stomach, how quickly it is acted upon by the digestive juices, and, finally, how much passes out undigested; points of great importance to the healthy system, but still more so to the system weakened by disease.

There are two ways of determining the digestibility of a food stuff in gastric juice. One consists in the introduction of a weighed amount of the substance into the stomach of a man or animal through a fistulous opening, and noting the length of time required for its solution; the other, in the use of an artificial gastric juice by which the amount of substance capable of being dissolved and digested in a given time can be quantitatively ascertained. The

first of these methods was made use of by Dr. Beaumont in his celebrated experiments on the Canadian, Alexis St. Martin, about 1830, and has been employed many times since with animals by other workers. While it would appear in some respects to be the better method, there are reasons why it is not so advantageous as the other, mainly because it is not capable of showing such small differences, it is not free from nervous influences and personal idiosyncrasies, and, lastly, it is less convenient. The method with artificial gastric juice, on the other hand, admits of the conditions being the same in each case, and since the digestion of a food is by itself simply a chemical process, it would seem better in a determination of *digestibility* that the process be shorn of all those conditions, natural or otherwise, which tend to interfere with the purely chemical action of the digestive juice.

Few experiments appear to have been made on the digestibility of fish; this is the more strange when we consider what an important item of food fish constitutes, particularly along our seaboard. Yet the idea is prevalent, based apparently on general grounds, that fish flesh is not easily digestible. Thus Maly[1] mentions that "fish flesh is difficult of digestion, although the reason is not known." Still, as Voit[2] remarks, "nothing certain is known regarding the digestibility of different kinds of flesh, although much is said concerning it. Probably digestibility is in part dependent upon the nature of the fat present and the manner of its distribution; thus the presence of a difficultly fusible fat with considerable stearin would tend to hinder digestibility (as in mutton); the same thing probably occurs when the contents of the sarcolemma are permeated with much fat (as in the lobster and eel.)" This statement at once suggests the probability of great variation in the digestibility of the flesh of any one species, dependent on a large number of conditions, which, in the case of fish particularly, are somewhat difficult of control; thus age, sex, food, period of spawning, length of time they have been preserved, are a few of the many natural conditions which would tend to modify the digestibility of the flesh and render generalisations from even a large number of results somewhat uncertain.

Still, as no systematic experiments appear ever to have been tried with fish flesh, we have attempted to obtain some positive results concerning the relative digestibility of the more common

[1] Hermann's Handbuch der Physiologie **5**, 112. [2] *Ibid.* **6**, 447.

edible species, as well as the general digestibility of fish as compared with beef, veal, lamb, etc.

The Method Employed.

The gastric juice.—For reasons already given, artificial digestion was chosen as the best adapted for the purpose, and with this end in view a gastric juice was needed which should be both constant in composition and activity during the length of time required for trying the experiments. A large quantity of so-called "pure pepsin"[1] was obtained, thoroughly sampled, and then placed in a tightly stoppered bottle and kept in a cool, dry place to prevent change. The acid used was pure hydrochloric of exactly 0.2 per cent. strength. From this material fresh gastric juice was made for each series of experiments, 5 grams of the pepsin being dissolved in 1 litre of the dilute acid. This furnished a digestive mixture of suitable strength, and, as subsequent experiments showed, well adapted to the purpose.

Preparation of the flesh.—In order that a fair sample of the flesh might be obtained in each case, 100 grams, freed from tendons, fat, skin and bones, were weighed off and finely divided by chopping. Small portions of the sample tissue were then taken for a determination of the amount of solid matter,[2] and then two portions of 20 grams each were weighed out to determine the digestibility. These two latter portions were placed in small porcelain mortars covered with watch glasses, and then set into a steam-bath heated by a large gas flame for 30 minutes. This bath was a small copper oven, on the bottom of which was a layer of water 1 or 2 inches in depth, while some distance above this was placed a perforated plate upon which the dishes were set, the whole provided with a tightly fitting cover, with a small outlet for the escaping steam. Heated in this for half an hour the fish or meat was thoroughly and evenly cooked without loss of any extractives, and being in mortars, the tissue after steaming could be ground up fine without loss. The flesh was then ready for digestion.

The digestion.—As already stated, two separate or duplicate determinations were made of each sample. Each portion of 20 grams was placed in a beaker with 200 cc. of the standard gastric juice, covered with a watch glass and set into a bath heated at 38–40° C.

[1] Manufactured by Henry Thayer & Co.

[2] Determined by simply drying at 100° C. until of constant weight.

for 22 hours with occasional stirring. This bath consisted of a metal box with a movable cover, and having about midway of its height a perforated plate upon which the beakers were placed. The bath was filled with water to such an extent that the beakers were immersed about half an inch. The space above, when the bath was closed, was of course saturated with aqueous vapor, and thus any evaporation of the contents of the beakers was prevented. The temperature was kept quite constant by a small gas flame, and the extreme variations were not more than 35–42° C., these occurring only during the night and early morning. The length of time the mixtures were heated, viz. 22 hours, was no longer than was necessary to insure accurate and concordant results. In an artificial digestion the accumulation of the products formed tends to retard the action of the fluid, but in no case were our results impaired by saturation of the digestive mixture, for that this could never have occurred ordinarily is plainly shown by the large amount of *blood fibrin* dissolved by the gastric juice in a trial experiment. The addition of larger amounts of flesh, moreover, in the case of fish, 30–40 grams, simply diminished the digestive action.

Determination of the amount digested.—This can be accomplished by either weighing the undigested residue, or by determining directly the amount dissolved. In a recent work by Jessen[1] on the influence of different modes of preparation on the digestibility of meat, the former method was used. Unless the amount of water contained in the meat experimented with, however, is determined, a very decided error may be introduced. Thus Jessen found by experiment with frogs' legs[2] that 2 grams of the raw flesh, introduced into the stomach of a dog, required on an average 4.46 hours for digestion, while the same amount of beef, similarly prepared, required on an average 5.58 hours, and thus from this experiment the relative digestibility of the two would be as 84 : 100. Our experiments, however, show quite a different result, easily explained by a determination of the percentage amount of solid matter in the two kinds of flesh. Thus, while 20 grams of beef contain on an average 5.1 grams of solid matter, the flesh of frogs' legs contains but 3.5 grams. It is evident from this example, then, that a determination of the total solid matter is necessary in each species of flesh; but even when that is done, and corrections made

[1] Zeitschrift für Biologie **19**, 130. [2] *Ibid.* p. 140.

accordingly, we have found a decided difficulty in filtering the digestive mixtures. The undissolved residue of the fish is so gelatinous that it is next to an impossibility to wash it entirely free from peptones. We, therefore, decided to work with the filtrate, and after several trials by precipitating the dissolved albumin with tannic acid, according to the method of Johnson,[1] and also by determining the specific gravity of the fluid after filtration, we finally adopted the following method, which has proved quite satisfactory. After the gastric juice has been allowed to act for the requisite length of time on the 20 grams of flesh the mixture is cooled to 20° C., and then diluted to 250 cc., in a graduated flask, with distilled water. After being thoroughly mixed it is filtered on a dry filter, and then 50 cc. or one-fifth of the entire mixture, is transferred by a pipette to a small weighed dish, and to it are added 5 cc. of a standard solution of sodium carbonate of such strength as exactly to neutralise the acid present. The fluid is then evaporated to dryness on the water-bath, and finally dried at 110° C. until of constant weight. In order that the results obtained may express the absolute amounts of matter dissolved by the gastric juice, it is necessary to carry on control experiments with the gastric juice itself. This is also desirable as a proof of the uniform strength of the gastric juice. Thus in each series of experiments 200 cc. of the standard juice were warmed at 38–40° C. for 22 hours, so that all albumin contained in the pepsin could be converted into peptone, then diluted to 250 cc. and 50 cc., neutralised, evaporated, and dried as already described. This residue, subtracted from the weight of the residue left by the evaporation of the 50 cc. of the digestive mixtures, multiplied by 5, gives quite accurately the amount of matter (peptones and intermediate products together with some salts) dissolved from the 20 grams of flesh. Theoretically there are one or two minor objections to this method, the most noticeable, perhaps, being the variable amount of undigested residue suspended in the fluid diluted to 250 cc. The amount of space, however, occupied by this matter is not large, and its influence on the accuracy of the method not great. Again, by the evaporation of the peptones, and drying at 110° C., there is doubtless some slight oxidation, but still it cannot be great, as the dried residue is soon brought to a constant weight. While the method seems longer than to weigh the undissolved residue, it is by far more accurate, and in the end we believe shorter.

[1] Bulletin de la Société chimique de Paris **23**, 40.

The fish experimented[1] with were obtained at a local market, and while always quite fresh and in good condition, we had no means of knowing how long they had been out of water.

In all of the experiments the flesh was cooked by steaming, unless otherwise expressed.

Tables I–V give all the data of the experiments, while table VI contains the average amounts digested of each sample of cooked flesh, together with the relative digestibility as compared with cooked (steamed) beef, taken as 100.

A glance at the results of the control analyses of the gastric juice alone plainly shows the constancy of its composition. The strength and activity of the digestive mixture, moreover, is easily seen from the amount of blood fibrin (Table IV) dissolved by 200 cc. of the fluid; an amount far in excess of the fish or beef dissolved by the same quantity of fluid.

The results of the analyses show plainly that the method adopted is as good as could be expected, for it must be remembered that the two results obtained from each sample of flesh are not merely from duplicated analyses, but from duplicated digestions as well, and in these, extending as they do over 22 hours, with slight variations in temperature and agitation, small differences are to be expected. The very great divergence noticed, however, in the results obtained from *different* samples of the same species of flesh show at once that there are other conditions, such as age, etc., which affect the digestibility of the flesh more or less, so that, in order to obtain results from which to draw strict generalisations, it would be necessary to experiment with fish of different species, of like age, sex, and reared under like conditions. As examples of this we have the very divergent results from two samples of veal, and also of two blue fish (88.69 and 73.44). As direct evidence that age, sex, etc., do exert a modifying influence on the digestibility of flesh, we have three experiments on the flesh of the lobster; one with a small young lobster, a second with a large female, and a third with a large male of the same species. The duplicate digestions gave fairly concordant results; the average relative digestibility being for the young specimen 87.81, for the large female 79.06, and for the male 69.13. This shows plainly some modifying influence in the flesh itself. In composition, so far as the solid matter is con-

[1] For composition of the fish experimented with, see "Zur Chemie der Fische," Berichte der deutsch. chem. Gesell. **16**, 1839, by Prof. W. O. Atwater.

TABLE I.

	FIRST SERIES. April 18.				SECOND SERIES. April 21.				THIRD SERIES. April 23.				FOURTH SERIES. April 25.				FIFTH SERIES. April 28.			
	Hippoglossus vulgaris. Halibut.		Hiatula onitis. Tautog.		Salvelinus fontinalis. Brook Trout.		Scomber scombrus. Mackerel.		Esox lucius. Pike.		Roccus Americanus. White Perch.		Pleuronectidae Americanus. Flat Fish.		Perca Americana. Yellow Perch.		Roccus lineatus. Striped Bass.		Salmo salar. Salmon.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Grams taken	5.8010	5.1408	6.6509	.4162	4.9927	5.4913	4.6668	5.9266	7.3142	4.8280	6.9013	6.1971	6.4699	7.2258	7.7499	8.3051	7.4441	7.2179	8.9633	9.5412
Gave dried residue	1.1857	1.0350	1.3703	1.3102	.9634	1.0703	1.1755	1.5316	1.4384	.9467	1.3497	1.2236	1.1081	1.2445	1.4029	1.5069	1.5497	1.4924	2.8687	2.9580
Per cent solid matter	20.43	20.13	20.60	20.60	19.49	19.67	25.18	25.84	19.66	19.61	19.55	19.74	17.09	17.22	18.10	18.14	20.81	20.66	32.00	31.00
Average per cent. solid matter	20.28		20.60		19.58		25.51		19.635		19.695		17.155		18.12		20.735		31.50	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
20 gr. sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	1.0070	1.0134	1.0223	1.0401	lost.	.9527	1.0201	1.0113	.9139	1.0540	.9102	.8950	.8437	.8641	.8962	.8905	.9612	.9764	1.0596	1.0206
200 cc. S.G. juice diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	0.3180				0.3178				0.3123				0.3126				0.3134			
Residue from digestion less the gastric juice residue	.6890	.6954	.7043	.7221	....	.6349	.7023	.6935	.6016	.7417	.5979	.5827	.5311	.5515	.5836	.5779	.6478	.6630	.7462	.7072
The above × 5 or the entire products of digestion from 20 gr.	3.4450	3.4750	3.5215	3.6105	....	3.1745	3.5115	3.4675	3.0080	3.7085	2.9895	2.9135	2.6555	2.7575	2.9180	2.8895	3.2390	3.3150	3.7310	3.5360
Average of the above	3.4600		3.5660		3.1745		3.4895		3.35825		2.9515		2.7065		2.9037		3.2770		3.6335	

TABLE II.

	SIXTH SERIES. April 30.				SEVENTH SERIES. May 2.				EIGHTH SERIES. May 5.				NINTH SERIES. May 5.				TENTH SERIES. May 12.			
	Sparus chrysops. Porgee.		Clupea sapidissima. Shad.		Lutjanus Blackfordi. Red Snapper.		Anguilla rostrata. Eel.		Beef.		Veal.		Gadus aeglefinus. Haddock.		Paralichthys dentatus. Flounder.		Bothus maculatus. Day Light.		Prionotus palmipes. Sea Robin.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Grams taken	7.6491	6.9193	8.2493	7.9472	6.8025	6.9713	6.5942	6.6020	5.4199	6.7188	6.2437	5.7730	6.9118	5.9901	6.9864	7.0080	6.6987	4.7163	6.3935	7.1382
Gave dried residue	1.7221	1.5647	2.6035	2.4791	1.5038	1.5406	1.4380	1.4375	1.3963	1.7681	1.5607	1.4395	1.2601	1.0941	1.6188	1.6065	1.2301	.8670	1.3676	1.5745
Per cent. solid matter	22.51	22.61	31.57	31.11	22.10	22.09	21.80	21.77	25.75	26.31	24.99	24.93	18.23	18.26	23.17	22.92	18.37	18.38	21.69	22.05
Average per cent. solid matter	22.56		31.335		22.095		21.785		26.035		24.96		18.245		23.045		18.375		21.87	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
20 gr. sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	1.0081	1.0215	1.0538	1.0254	.9707	.9837	.9004	.8959	1.1404	1.1355	1.1553	1.1436	.9841	.9850	1.0090	1.0058	.8949	.8904	.9293	.9571
200 cc. standard gastric juice diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	0.3105				0.3164				0.3146				0.3169				0.3141			
Residue from digestion less the gastric juice residue	.6976	.7110	.7433	.7149	.6543	.6673	.5840	.5785	.8258	.8209	.8407	.8290	.6672	.6681	.6921	.6889	.5808	.5763	.6152	.6477
The above × 5 or the entire products of digestion from 20 gr	3.4880	3.5550	3.7165	3.5745	3.2715	3.3365	2.9200	2.8925	4.1290	4.1045	4.2035	4.1450	3.3360	3.3405	3.4605	3.4445	2.9040	2.8815	3.0760	3.2385
Average of the above	3.5215		3.6455		3.3040		2.9062		4.1167		4.1742		3.3382		3.4525		2.8927		3.1572	

TABLE III.

	ELEVENTH SERIES. May 14.				TWELFTH SERIES. May 19.				THIRTEENTH SERIES. May 19.				FOURTEENTH SERIES. May 22.				FIFTEENTH SERIES. June 2.			
	Salmo salar. Salmon.		Gadus callarias. Cod.		Coregonus clupeiformis. Lake White.		Homarus Americanus. Lobster. Young.		Crab.		Pomatomus saltator. Blue Fish.		Cynoscion regale. Weak Fish.		Veal.		Clupea harengus. Herring.		Stromateus triacanthus. Butter Fish.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Grams taken	4.3430	4.8259	5.5381	5.8758	6.3449	4.9515	3.3703	2.8816	5.1634	5.0654	6.6347	5.6929	5.6586	5.6039	5.4457	4.4465	5.5057	4.7300	4.8831	3.7325
Gave dried residue	1.3383	1.5110	1.0194	1.0684	1.6253	1.2639	.7300	.6297	1.2195	1.1922	1.2901	1.1109	1.1279	1.1066	1.3332	1.0719	1.3483	1.1500	1.1186	.8513
Per cent. solid matter	30.81	31.31	18.40	18.18	25.61	25.52	21.66	21.85	23.61	23.53	19.42	19.51	19.93	19.64	24.48	24.10	24.47	24.52	22.97	22.81
Average per cent. solid matter	31.06		18.29		25.565		21.755		23.57		19.465		19.785		24.29		24.495		22.89	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
20 gr. sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	1.0663	1.0495	.8922	.9015	1.0826	1.0842	1.0153	1.0388	.8621	.8591	.8712	.9421	.9090	lost.	1.0132	1.0397	.9780	.9811	.9570	.9644
200 cc. standard gastric juice 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	0.3110				0.3164				0.3123				0.3154				0.3137			
Residue from digestion less the gastric juice residue	.7553	.7385	.5812	.5905	.7662	.7678	.6989	.7224	.5498	.5368	.5589	.6298	.5836	.....	.6978	.7143	.6643	.6674	.6343	.6507
The above × 5 or the entire products of digestion from 20 gr.	3.7765	3.6925	2.9060	2.9525	3.8310	3.8390	3.4945	3.6120	2.7490	2.6840	2.7945	3.1490	2.9180	.....	3.4890	3.5215	3.3265	3.3370	3.1715	3.2535
Average of the above	3.7345		2.9292		3.8350		3.5532		2.7165		2.9717		2.9180		3.5052		3.3317		3.2125	

TABLE IV.

	SIXTEENTH SERIES. May 7.				SEVENTEENTH SERIES. June 2.				EIGHTEENTH SERIES. June 2.				NINETEENTH SERIES. June 3.				TWENTIETH SERIES. June 16.			
	Serramis atrarius. Sea Bass.		Serramis atrarius. Sea Bass		Beef.		Beef.		Clupea sapidissima. Shad. Dark meat.		Clupea sapidissima. Shad. White meat.		Beef.		Beef.		Lobster. Large Male.		Blood	Fibrin.
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*		
Grams taken	5.2485	6.0050	.....	.....	5.8633	5.7788	.....	.....	4.0414	4.4600	6.6883	5.1362	4.6522	5.0094	.....	.....	4.6161	5.1282	.....	.....
Gave dried residue	1.1153	1.2872	.....	.....	1.4781	1.4471	.....	.....	1.3118	1.4640	2.0627	1.5359	1.2089	1.2842	.....	.....	.9643	1.0610	.....	.....
Per cent. solid matter	21.24	21.10	.....	.....	25.20	25.04	.....	.....	32.46	32.81	30.84	29.93	25.75	25.63	.....	.....	20.89	20.64	.....	.....
Average per cent. solid matter	21.17		21.17		25.12		25.12		32.63		30.38		25.69		25.69		20.76			
	20 gr.	20 gr.	30 gr.	40 gr.	20 gr.	20 gr.	20 gr. raw.	30 gr. raw.	20 gr.	20 gr.	20 gr.	20 gr.	20 gr. raw.	20 gr. raw.	20 gr.	20 gr.	20 gr.	20 gr.	Added indef. quant.	
Sampled flesh and 200 cc. S.G.J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	.9919	.9999	.9625	.8200	1.1476	1.1493	1.1920	1.4685	1.0290	1.0225	1.1156	1.0867	1.1329	1.1244	1.0668	1.1032	.8325	.9141	1.9238	.....
200 cc. standard gastric juice diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	0.3160				0.3163				0.3141				0.3128				0.3141			
Residue from digestion less gastric juice residue	.6759	.6839	.6465	.5040	.8313	.8330	.8757	1.1522	.7049	.7084	.8015	.7726	.8201	.8116	.7540	.7904	.5184	.6000	1.6097	.....
The above × 5 or the entire products of digestion from 20 gr.	3.3795	3.4195	3.2325	2.5200	4.1565	4.1650	4.3785	5.7610	3.5245	3.5420	4.0075	3.8630	4.1005	4.0580	3.7700	3.9520	2.5920	3.0000	8.0485	.....
Average of the above	3.3995		3.2325	2.5200	4.1607		4.3785	5.7610	3.5332		3.9352		4.0792		3.8610		2.7960		8.0485	

TABLE V.

	TWENTY-FIRST SERIES June 4.				TWENTY-SECOND SERIES. June 9.				TWENTY-THIRD SERIES. June 16.				TWENTY-FOURTH SERIES. June 18.			
	Lamb.		Mutton.		Pomatomus saltator. Blue Fish.		Pomatomus saltator. Blue Fish.		Light meat of Spring Chicken.		Dark meat of Spring Chicken.		Frog Legs.		Lobster. Large Female.	
	a	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
Grams taken	4.4828	5.1652	5.2508	4.7776	5.1936	5.8776	.....	.....	4.7043	4.6394	4.3887	4.6880	5.1115	3.6942	4.3595	4.7139
Gave dried residue	1.3533	1.5272	1.6352	1.4594	1.0328	1.1639	.....	.....	1.2518	1.2384	1.1585	1.2742	.9105	.6618	.9238	1.0080
Per cent. solid matter	30.18	29.56	31.14	30.54	19.88	19.80	.....	.....	26.60	26.69	26.39	27.01	17.81	17.91	21.19	21.39
Average per cent. solid matter	29.87		30.84		19.84		19.84		26.645		26.70		17.86		21.29	
	a	*b*	*a*	*b*	*a* raw.	*b* raw.	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*
20 gr. sampled flesh and 200 cc. S. G. J. 22 hrs. at 40°—diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	1.0313	1.0201	1.0753	1.0444	1.0632	1.0713	1.0412	1.0239	1.0308	1.0010	.9991	.9955	.9724	.9611	.9575	.9541
200 cc. standard gastric juice diluted to 250 cc. 50 cc. of this + 5 cc. Na_2CO_3 gave dried residue	0.3141				0.3149				0.3141				0.3160			
Residue from digestion less the gastric juice residue	.7179	.7060	.7612	.7303	.7483	.7564	.7264	.7090	.7167	.6869	.6850	.6814	.6564	.6451	.6415	.6381
The above × 5 or the entire products of digestion from 20 gr.	3.5860	3.5300	3.8060	3.6515	3.7415	3.7820	3.6320	3.5450	3.5835	3.4345	3.4250	3.4070	3.2820	3.2250	3.2075	3.1905
Average of the above	3.5580		3.7287		3.7617		3.5885		3.5090		3.4160		3.2535		3.1990	

TABLE VI.

Average results from each sample of cooked flesh.

	Percentage solid matter.	Solid matter in 20 grams.	Average amount digested from 20 grams.	Relation of the amounts digested to the amount digested from 20 grams cooked beef = 4.0461.
Beef	25.12	5.024	4.1607	
Beef	26.03	5.206	4.1167	= 100.00
Beef	25.69	5.138	3.8610	
Veal	24.96	4.992	4.1742	
Veal	24.29	4.858	3.5052	= 94.89
Mutton	30.84	6.168	3.7287	92.15
Lamb	29.87	5.974	3.5580	87.93
Spring chicken (light meat)	26.64	5.328	3.5090	86.72
" (dark meat)	26.70	5.340	3.4160	84.42
Lake White (Coregonus clupeiformis)	25.56	5.112	3.8350	94.78
Shad (Clupea sapidissima)	31.33	6.266	3.6455	90.09
" " (light meat)	30.38	6.076	3.9352	97.25
" " (dark meat)	32.63	6.526	3.5332	87.32
Salmon (Salmo salar)	31.06	6.212	3.7345	92.29
" "	31.50	6.300	3.6335	89.80
Tautog (Hiatula onitis)	20.60	4.120	3.5660	88.13
Porgee (Sparus chrysops)	22.56	4.512	3.5215	87.03
Blue fish (Pomatomus saltator)	19.84	3.968	3.5885	88.69
" "	19.46	3.892	2.9717	73.44
Mackerel (Scomber scombrus)	25.51	5.102	3.4895	86.24
Halibut (Hippoglossus vulgaris)	20.28	4.056	3.4600	85.51
Flounder (Paralichthys dentatus)	23.04	4.608	3.4525	85.32
Sea Bass (Serranus atrarius)	21.17	4.234	3.3995	84.01
Pike (Esox lucius)	19.63	3.926	3.3582	82.99
Haddock (Gadus aeglifinus)	18.24	3.648	3.3382	82.50
Herring (Clupea harengus)	24.49	4.898	3.3317	82.34
Striped Bass (Roccus lineatus)	20.73	4.164	3.2770	80.99
Red Snapper (Lutjanus Blackfordi)	22.09	4.418	3.3040	81.65
Trout, brook (Salvelinus fontinalis)	19.58	3.916	3.1745	78.45
Sea Robin (Prionotus palmipes)	21.87	4.374	3.1572	78.03
White Perch (Roccus Americanus)	19.69	3.938	2.9515	72.94
Fresh Cod (Gadus callarias)	18.29	3.658	2.9292	72.39
Weak fish (Cynoscion regale)	19.78	3.956	2.9180	72.11
Yellow fish (Perca Americana)	18.12	3.624	2.9037	71.76
Eel (Anguilla rostrata)	21.78	4.356	2.9062	71.82
Window Pane (Bothus maculatus)	18.37	3.674	2.8927	71.49
Flat fish (Pleuronectidae Americanus)	17.15	3.430	2.7065	66.89
Lobster (young)	21.75	4.350	3.5532	87.81
" (large female)	21.29	4.258	3.1990	79.06
" (large male)	20.76	4.152	2.7960	69.13
Crab	23.57	4.714	2.7165	67.13
Frogs' legs	17.86	3.572	3.2535	80.46

cerned, there was no appreciable difference in the three samples. Bearing in mind, however, these possible variations, it is very evident from our results that the average digestibility of fish flesh is far below that of beef similarly cooked. In but two instances, in the case of shad and lake white, does the digestibility of fish flesh approach that of beef, although, from the average of our experiments, several are as easily digestible as mutton, lamb and chicken.

Pavy[1] states that fish with white flesh, such as the whiting, etc., are less stimulating and lighter to the stomach, or more easy of digestion, than fish with more or less red flesh, as the salmon. Our experiments confirm this statement so far as digestibility is concerned. Thus the average digestibility of the salmon and trout is considerably below the average of the more digestible white fish. The difference between the digestibility of the light and dark meat of the same fish is somewhat striking, as in the case of the shad, where the digestibility of the former was found to be 97.25, as compared with beef, while the dark flesh was 87.32. A similar difference, though very much smaller, is to be noticed between the light and dark meat of the chicken.

This difference in digestibility is in part due, without doubt, to the amount of fat present, for, as Pavy states, in the flesh of white fish there is but little fat, it being accumulated mainly in the liver of the animal, while in red fish there is more or less fatty matter incorporated with the muscular fibres. For a similar reason eels, mackerel and herring are, according to Pavy, less suited to a delicate stomach than some of the white fish, and our experiments show that in digestibility two of them stand below the more digestible white fish; mackerel, however, from our single experiment with the white portion of the flesh, showed a comparatively high digestibility. In all of our experiments, however, with white fish, we rejected the outer layer of dark flesh, except in the case of the shad. The varying differences in digestibility are not to be considered as due wholly to differences in the amount of fat in the flesh; thus the flesh of fresh cod contains but little fat, and yet it is one of the most indigestible of the white fish experimented with. This agrees with Pavy's[2] experience "that it is a more trying article of food to the stomach than is generally credited." Again Pavy[3] makes the following statement, based on his experience in fish dietetics, "of all fish, the whiting may be regarded as the most delicate, tender and

[1] On food and dietetics, Amer. ed., 1874, p. 171. [2] *Loc. cit.* p. 173. [3] *Loc. cit.* p. 172.

easy of digestion." "The haddock is somewhat closely allied, but is inferior in digestibility," while "the flounder is light and easy of digestion, but insipid." With all these statements our results agree perfectly, assuming the lake white of our experiments to be analogous to the English whiting.

Maly,[1] in speaking of the digestive processes in the living stomach, says that raw flesh is more slowly digested than cooked, probably for the reason that with dilute acids the coagulated albumin of cooked flesh is more easily converted into acid albumin. Likewise, that the flesh of young animals is more rapidly digested than that of older, while fat flesh is but slowly attacked, as the melted fat surrounds the muscle fibres. With reference to the first of these statements, Jessen[2] found, by experimenting with perfectly lean beef of known age, that he had only a small undigested residue in an artificial digestion of the raw beef, but with the same amount of partially boiled beef a much larger amount remained undigested, and when thoroughly boiled a still larger residue was found. Taking the amount of undigested residue as a measure of the digestibility, the proportion with the same sample of beef was as follows: raw beef 100, partially boiled 167, thoroughly boiled 317. The gastric juice employed by Jessen, however, could hardly be considered as made up of a dilute acid, containing, as it did, 2.5 and 5.0 per cent. of concentrated hydrochloric acid.

In our own experiments, with a gastric juice containing but 0.2 per cent. of pure hydrochloric acid, positive results were obtained as follows:

	1st sample of Beef.		*2d sample of Beef.*	
	Raw.	Cooked (steamed).	Raw.	Cooked (steamed).
Amount digested from 20 grams,	4.0792	3.8610	4.3785	4.1607
Relative proportion,	100.0	94.65	100.0	95.04

The difference here, then, is not so great, though sufficiently pronounced to indicate plainly the influence of cooking.

A similar experiment with a sample of blue fish gave a like result:

	Raw.	Cooked (steamed).
Amount digested from 20 grams,	3.7617	3.5885
Relative proportion,	100.0	95.39

[1] Hermann's Handbuch der Physiologie **5**, 111.

[2] Zeitschrift für Biologie **19**, 128.

With the *raw beef*, however, digestion was so near complete that a second experiment was tried with a larger quantity, as follows:

	From 20 grams.	From 30 grams.
Amount digested (raw beef),	4.3785	5.7610
Relative proportion,	100.0	131.57

This would make the relative digestibility of cooked (steamed) and raw beef as 100.0 : 142.38, a difference nearly as great as that found by Jessen between raw and partially boiled beef. It is plain, then, that the digestibility of *raw* beef is considerably greater than cooked.

Whether the relative digestibility of raw and cooked fish, given above, would be changed by increasing the amount of flesh added, we cannot say. It is a point of little importance, but from the following experiment with cooked fish it probably would make but little difference. This experiment with cooked *sea bass* was tried mainly to ascertain the quantity of flesh best adapted to 200 cc. of our standard gastric juice:

	From 20 grams.	From 30 grams.	From 40 grams.
Amount digested,	3.3995	3.2325	2.5200
Relative proportion,	100.0	95.08	74.12

In this case, increasing the amount of material plainly diminishes the digestive action.

With regard to the second statement of Maly's, above quoted, our experiments tend to show that, in some instances at least, the flesh of younger animals is less easily digestible than that of older animals of the same species. This is well illustrated in the greater digestibility of mutton as compared with lamb.

AN IMPROVEMENT IN THE APPARATUS USED FOR PRECIPITATING COPPER BY ELECTROLYSIS.

By Herbert C. Foote.

Those who have occasion to make many determinations of copper by the electrolytic method have undoubtedly experienced some difficulty in always obtaining a current of proper strength, and, when the battery is to be used for two or three consecutive days, of keeping it so without changing the battery fluids.

I have devised a simple piece of apparatus which has saved me much trouble in this line, and as it has worked with extreme satisfaction in my laboratory for the past year, I beg leave to suggest its trial, at least, by those who have many copper determinations to make.

The platinum dishes are arranged on a board as shown in section by Fig. 2. The current from the battery, which is kept in a room in the basement, is carried by insulated wires to the laboratory, and made to pass through a certain number of coils of fine insulated iron wire before it passes to the platinum dishes.

Fig. 1 shows the under side of the board with the resistance coils and connecting wires sunken into it, so that no wires are visible above the board save the ones connected to the platinum strips dipping into the dishes.

The current enters at *a* and passes to *c*, where it enters a switch from which it may be made to pass directly to a switch at *g*, or it may be made first to traverse either one of the coils *m*, *n*, on its way, by a simple movement of the switch handle above the board. From *g* it may be made to pass through *h* to the switch at *r*, or by connecting the switch with *i*, *k* or *l*, the current will first traverse one, two or all of the coils *o*, *p*, *q*, and when it reaches *r* it will have the required strength. The coils have the following lengths of fine iron wire respectively: *m*, 1½ metres; *n* and *o*, 3 metres each; *p* and *q*, 4½ metres each.

More coils may be added if it is desirable, but with the arrangement shown in the cut a resistance of 1½ metres may be obtained, which may be increased, by additions of 1½ metres each, up to 15 metres, by properly manipulating the switches *c* and *g*. For example, if the switch *c* be connected with *e*, and the switch *g* with *i*, the current will pass through 4½ metres of the iron wire.

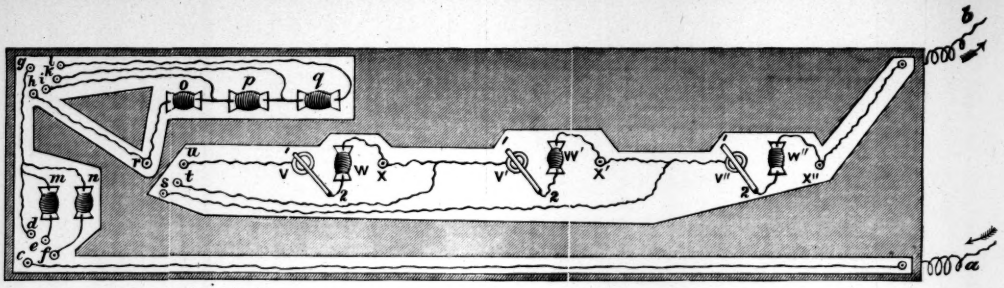


FIG. 1.—VIEW OF BOTTOM OF BOARD SHOWING THE RESISTANCE COILS AND CONNECTIONS FOR THREE DISHES.

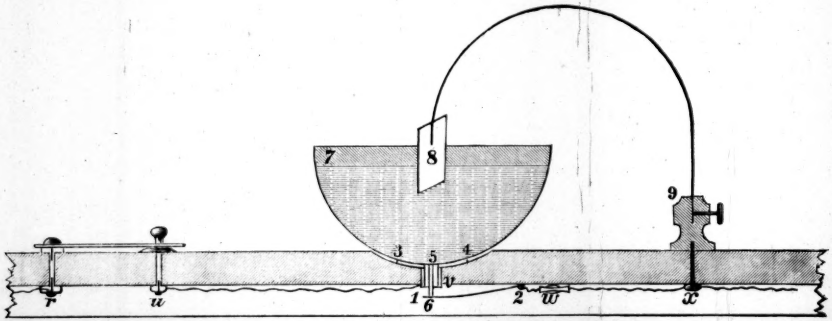


FIG. 2.—SECTION SHOWING ONE DISH IN POSITION.

The board shown in the cut is arranged for only three dishes, but it will be readily seen that any number might be added. As the battery grows weaker, or as dishes are removed or added to the circuit, the strength of the current is kept uniform by manipulating the switches. This might be made to work automatically.

The switch r with its connections s, t and u make it possible to use one, two or all of the dishes. If only one dish is to be used, the connection is made with s, and the current passes through the cylindrical copper connection v'' (see also Fig. 2, v) to the platinum and finally through x'' to b. If two dishes are to be used, the switch r is connected with t, and the current passes first to the dish over v', thence through the platinum strip to x' and then to the second dish over v''. When all the dishes are to be used, connection must be made with u.

The method of automatically regulating the current in the case of removing a dish from the circuit is shown by Fig. 2. A coil of fine iron wire w, equal to the resistance of the solution in a dish, is placed under the board and near each dish. Through the centre of the piece of platinum 3, 4, upon which the precipitating dish rests when in connection with the current, is a small hole, which is continued down through the board and lined with a piece of copper pipe v, which is soldered to the platinum to make the connection. A short stick of wood 5, 6, passes through this pipe and is so arranged with a spring 1, 2, that when the resistance coil w is in the circuit, the stick protrudes slightly above the platinum foil. When, however, a dish is placed upon the board, it pushes down, by its weight, the stick 5, 6, removing the strip 1, 2, from contact with v, thus disconnecting the resistance coil and at the same time causing the current to pass from v through the solution and platinum strip to x. When a dish is removed, the current through 8, 9, is of course broken, and the spring 1, 2, comes in contact with v making the connection with the resistance coil, which, being equal to the resistance in the dish, keeps the current the same in the other dishes.

If two dishes are to be used, and the solution is only ready for one, the switch r is connected with t, and the dish which is ready is placed on the platinum above v''. The current will then pass from t to v', and through the strip 1, 2, to the resistance coil w', and thence through x' to v'', and finally through the liquid to x'' and b. When ready to add the second dish to the circuit, it may be

done by simply placing the dish in its place over v', when it will automatically disconnect the resistance coil w', and the strength of the current will remain the same and sufficient for both dishes. Either one of the two dishes may now be removed at any time without altering the strength of the current, or in any way interfering with the work of the other dish in the circuit. The third dish may also be added at any time by simply changing the switch r from t to u and manipulating the switches c and g so as to increase the current sufficiently. In the same manner, any number of dishes may be used.

The strength of the current may be ascertained by passing it through acidulated water in an inverted tube graduated in cc. and noting the amount of mixed gases liberated in a minute; but I have found that a very little experience will enable one to tell when the current is suitable, by simply noting the rapidity with which the gas bubbles come off from the platinum strips in the liquid to be decomposed.

With the large number of determinations I have to make I find this arrangement of apparatus to be a great saving of time, and am sure it would be both neat and advantageous where only few analyses are to be made, and very desirable in the laboratory of a scientific school or college.

SYNTHETICAL RESEARCHES IN THE GLUCOSIDE GROUP.[1]

III.

By Arthur Michael.

Identity of Natural and Synthetical Methylarbutin.

Several months after my note on synthetical methylarbutin appeared in the *Journal of the German Chemical Society*, H. Schiff obtained the natural compound in a pure state, and found in regard to melting point and water of crystallisation, that slight

[1] This Journal **1**, 304; **3**, 171.

differences exist between it and the synthetical product. This has led me to prepare the synthetical product in larger quantities than hitherto, and carefully compare its properties with those of the natural product. The methylarbutin used for this purpose was prepared from methylhydroquinol, obtained by the action of methyl iodide on hydroquinol, and was converted into the glucoside by the method already described in my previous paper. I also prepared methylarbutin from natural arbutin, according to the excellent method described by H. Schiff.[1]

The melting point of the synthetical methylarbutin analysed by me was at 169°. I find that repeated crystallisation of the synthetical product from water gives a methylarbutin melting at 174·5°–175·5°, and that natural arbutin, prepared according to Schiff's method, melted exactly at the same temperature.[2]

The following results were obtained in the analysis of synthetical methylarbutin melting at 174·5°–175·5°:

0.2685 gram of substance, dried at 120°, gave 0.5346 gram of CO_2 and 0.1546 gram of H_2O.

	Theory for $C_6H_{11}O_5-O-C_6H_4OCH_3$.	Found.
C	54·54	54·3
H	6.29	6.4

For ascertaining the water of crystallisation the substance was dried by exposure to the air, then at 100°, and finally at 120°.

0.4668 gram of air-dried substance lost 0.0286 gram of H_2O.

0.5285 gram of air-dried substance lost 0.03118 gram of H_2O.

	Theory for $C_{13}H_{18}O_7+H_2O$.	Found.	
H_2O	5·9	6.1	5·9

[1] Annalen der Chemie **221**, 366.

[2] The somewhat lower melting point given in my first paper is explained by the small quantity of synthetical methylarbutin at my disposal, which prevented repeated crystallisation. As an illustration of how an almost inappreciable amount of impurity may lower a melting point, I will state my recent experience with thiocarbanilide. Mr. G. M. Palmer and myself lately prepared this substance from phenylmustard oil and aniline, and found its melting point to be at 153°. The fact that the melting point hitherto given was at 144°, and that probably no organic substance has passed through the hands of a greater number of chemists, induced me to ascertain whether this carbanilide obtained from carbon disulphide and aniline is really the same compound. I found that eight crystallisations from absolute alcohol raised the melting point from 144° to 151°. It is evident that an impurity contained in carbon disulphide—I believe that none of the known methods of purification eliminate it completely—unites with aniline to form a compound having much the same solubility as thiocarbanilide. I shall endeavor to obtain the by-products of the carbon disulphide manufacture, and make them the subject of a chemical investigation.

This agrees with the result obtained by Schiff from natural methylarbutin.[1]

It is also worthy of notice that synthetical methylarbutin, like the natural product, crystallises at times from very concentrated aqueous solutions in anhydrous crystals.

A further confirmation of the identity of the two products will be found in their behavior towards polarised light. The aqueous solutions of synthetical and natural arbutin turn the plane of polarisation to the left, and, apparently, to an equal degree.[2]

I believe the above-described experiments prove beyond a doubt that methylarbutin obtained by the action of acetochlorhydrose on potassium methylhydroquinol, and methylarbutin obtained according to Schiff's method from natural arbutin, are identical products.

That methylarbutin is contained in arbutin is rendered probable by these experiments, and placed almost beyond question by the recent research of Schiff,[3] who treated the natural product with benzylchloride and then succeeded in separating methylarbutin by crystallisation. Habermann's[4] paper may be considered as again showing the impossibility of separating arbutin from methylarbutin by crystallisation.[5]

[1] In the former analysis 3.5 per cent. of water was found. The substance analysed stood for upwards of a month in a room where the temperature frequently rose to 30° C., and there is no doubt that methylarbutin loses part of its water of crystallisation under these conditions.

[2] The instrument at my disposal was not sufficiently delicate to give the readings a scientific value. Tubes of equal length, containing equal quantities of the two products, could be interchanged in it without a noticeable change in the color of the disk.

[3] Annalen der Chemie **221**, 366. [4] Monatshefte für Chemie **4**, 759.

[5] J. Habermann has criticised my remarks on the constitution of arbutin in a very peculiar manner, and I take this opportunity of calling attention to it. I give the following as an illustration of Habermann's treatment of the work of other chemists: "He observed that methylarbutin does not melt at 175°, nor at 142°, as Schiff (Berichte **15**, 1842) has found, but at 169°; and also that the synthetical product is not colored by iron trichloride, whereas Schiff observed this property of all his crystallisations. It is not an easy matter to follow Michael in the statement: 'Die Eigenschaften (welche?) des Methylhydrochinons [Habermann has omitted glucoside, probably by mistake] scheinen mir entschieden für die Auffassung zu sprechen, dass das Arbutin ein Gemenge von Hydrochinon- und Methylhydrochinon-Glucosiden bildet.'"

This should be read with the following comment: Firstly, that synthetical methylarbutin agreed in its properties with natural arbutin, excepting in its behavior towards iron trichloride. Secondly, that I showed this property to be in accordance with our present knowledge of the behavior of iron trichloride towards aromatic phenols, and anticipated Schiff's proof, in a paper quoted by Habermann, who subsequently showed that iron trichloride gives no coloration with pure natural methylarbutin. Thirdly, that Schiff in the same paper showed the melting point of methylarbutin to be at 175°, and that his previous melting point—142°—was that of a mixture of arbutin and methylarbutin. Fourthly, that Schiff's paper appeared ten months later than my own, and it is, perhaps, excusable that I did not anticipate his correcting the melting point of methylarbutin from 169° to 175°. Fifthly, that several months before Habermann's paper appeared I expressed, in view of Schiff's results, the following determination: "I will prepare both products and carefully compare their properties" (this Journal **5**, 179).

Guaicol-glucoside.

The occurrence of methylarbutin in nature made it of interest to prepare glucosides synthetically which are isomeric with that compound. I have succeeded in preparing the glucoside of methylcatechol, while all experiments to obtain the corresponding resorcinol compound were without result.

Guaicol was prepared from the crude oil according to the directions given by Hlasiwetz,[1] and converted into the potassium derivative. Equivalent weights of the vacuum-dried salt and acetochlorhydrose were dissolved in absolute alcohol, the cold solutions mixed, and allowed to stand for three days. The deposition of salt began soon after mixing, and at the same time a perceptible odor of acetic ether became noticeable. The filtered solution was evaporated by exposure to the air, and after standing a long time partially solidified to form long needles. These were pressed between filter-paper, and crystallised four times from water.

An analysis gave the following results:

0.2274 gram of substance, dried at 120°, gave 0.4569 gram of CO_2 and 0.1326 gram of H_2O.

Theory for $C_6H_{11}O_5-O-C_6H_4OCH_3$.		Found.
C	54.54	54.79
H	6.29	6.48

Guaicol-glucoside crystallises from water as fine, white needles, forming globular clusters. It is very soluble in hot water, moderately in cold. Sparingly soluble in cold alcohol, hot alcohol dissolves it more easily, and the glucoside separates from the solution as arborescent groups of needles. The crystals are sparingly soluble in hot benzene, and insoluble in ether. It melts at 156½°–157°, and has a very bitter taste. The glucoside is not decomposed by boiling with an aqueous solution of silver nitrate, nor by Fehling's solution. Heated with dilute caustic potash it decomposes into guaicol and dextrose only when heated for some hours. Dilute acids effect this decomposition almost immediately. The aqueous solution of the glucoside gives no coloration with iron trichloride.

The formation of guaicol-glucoside may be represented as follows:

$$C_6H_4OCH_3OK + C_6H_7O_5Cl(OCCH_3)_4 + 4C_2H_5OH = C_6H_4\begin{matrix}O-CH_3\\O-C_6H_{11}O_5\end{matrix} + KCl + 4CH_3COOC_2H_5.$$

[1] Annalen der Chemie **106**, 365.

Eugenol-glucoside.

This compound is obtained by the action of acetochlorhydrose on potassium eugenol. The potassium derivative was prepared by dissolving potassium hydrate in a small amount of absolute alcohol, and adding the equivalent of eugenol to the solution. The crystalline salt, which separated from the mixture, was filtered, washed with absolute alcohol, pressed between bibulous paper, and dried *in vacuo*. A mixture of absolute alcoholic solutions of this salt and acetochlorhydrose, in equivalent proportions, was allowed to stand three days at the ordinary room-temperature, filtered from potassium chloride, and the filtrate evaporated by exposure to the air. After some days—from three to fourteen—the residue solidified to clusters of needles. These were pressed out and crystallised five times from water.

An analysis gave the following results:

0.2758 gram of substance, dried at 110°, gave 0.596 gram of CO_2 and 0.1717 gram of H_2O.

	Theory for $C_{16}H_{22}O_7$.	Found.
C	58.89	58.93
H	6.74	6.92

The formation of eugenol-glucoside is represented by the equation:

$$C_6H_3\begin{matrix}OK\\C_3H_5\end{matrix}OCH_3 + C_6H_7O_5Cl(OCCH_3)_4 + 4C_2H_5OH =$$

$$C_6H_4\begin{matrix}O-C_6H_{11}O_5\\OCH_3\\C_3H_5\end{matrix} + KCl + 4C_2H_5COOC_2H_5.$$

Eugenol-glucoside crystallises from water in white needles, melting at 132°. It is readily soluble in hot absolute alcohol, moderately in cold, and is insoluble in boiling ether and cold benzene. It dissolves in hot benzene and separates on cooling as a gelatinous mass, which has the same melting point as the crystalline substance. The aqueous solution reduces Fehling's solution on long boiling, but does not reduce an ammoniacal solution of silver nitrate; the addition of caustic potash to the solution, however, after heating a short time, causes the formation of metallic silver. Dilute acids decompose the glucoside readily into dextrose and eugenol.

TUFTS COLLEGE, MASS., *Nov. 17th*, 1884.

Contribution from the Chemical Laboratory of Cornell University.

I.—THE BEHAVIOR OF IODIC ACID AS AN INDICATOR.

By F. E. Furry.

It is known that when free iodic and hydriodic acids are brought together in the proportion of one molecule of the former to five of the latter, a decomposition sets in which results in the liberation of all the iodine present in both acids. Consequently, if to a solution containing the neutral salts of these two acids in excess, some other acid which will displace them be added, the iodine set free will indicate the amount of the acid added.

This reaction[1] may be used for the purpose of an indicator in volumetric analysis, since the titration of the liberated iodine can be effected by sodium hyposulphite and starch, and thus the amount of acid brought in contact with the salts containing iodine be determined by one of the sharpest end-points known in volumetric analysis.

While employed, under the direction of Dr. Caldwell, in estimating small amounts of sulphuric acid by the application of this method as suggested by Kjeldahl,[2] the singular recurrence of the blue color after its discharge by hyposulphite came to notice, and was ascribed for some time to atmospheric carbonic acid, and to carbonic acid probably present in small quantities in the reagents and water used.

Kjeldahl's express statement[3] to this effect has not been substantiated. While carbonic acid is known to bring about a slow liberation of iodine, experiments go to show that another cause is also operative.

With the supposition that the after-coloration was due to this acid alone, experiments were undertaken for the purpose of learning what other interferences, if any, are to be avoided, and how far the method is applicable.

A solution of sulphuric acid was accordingly made up, which contained 2.638 mgs. H_2SO_4 in every cc. A solution of sodium

[1] Mohr, Titrirmethode, 315.
[2] Fres. Zeit. Bd. **22.**
[3] Reper. der anal. Chemie, III Jahr. 268.

hyposulphite was also prepared by dissolving, approximately, 12.4 grams of the crystallised salt in a litre of water, and finally 8 grams potassium di-iodate (no neutral iodate being at hand) were dissolved in 200 cc. water and exactly neutralised with ammonia.

(1) *Delicacy of the end-point.* In order to ascertain the amount of acid necessary to produce a visible change in a neutral solution, in the absence of all interfering agents, 100 cc. freshly boiled distilled water, a small crystal of potassium iodide, 2 cc. of the iodate solution and a few drops of dilute sago paste were brought together in an Erlenmeyer flask. The mixture was perfectly colorless. As soon as the iodide was in solution, one drop (= .08 mg. H_2SO_4) was found to cause the liberation of sufficient iodine to change the liquid to a decided blue, and a like quantity of hyposulphite sufficed to discharge the color. It was not found difficult to pass back and forth in this way three times with .1 cc. standard acid. The delicacy of the end-point is seen to be much greater than that of many indicators in common use.[1]

(2) *Influence of dilution.* 20 cc. acid (= 52.76 mgs. H_2SO_4) were brought into varying amounts of water, and a small crystal of iodide and 2 cc. iodate added. The titration with hyposulphite was nearly completed before the addition of starch; in this way the end-point can be approached to within 2 cc. without hesitation, and the flocks of iodised starch which are sometimes formed in the presence of a large excess of iodine, and which are as good as inaccessible to hyposulphite, are entirely avoided.

Experiment.	Cc. Water added.	Cc. Hyposulphite, immediately.	Additional cc. Hypo. in 15 min.
(a)	...	...	...
(b)	50	21.30	.05
(c)	100	21.21	.12
(d)	150	21.20	.15
(e)	400	20.60	.30
(f)	400	20.85	.15

In (a) the reading was not possible on account of the intervention of a brick-red color between the blue and colorless states, due, no doubt, to the presence of excess of iodide. If a true end-point could have been found, it is doubtful if it would have been of any value, on account of the fact that iodine vapors were distinctly

[1] Thompson, Chem. News **47**, 124.

seen above the solution. In (b) the red coloration was not present, but iodine vapor and odor could be faintly recognised after titration; no odor was recognised in the others. In (f) 8 cc. of iodate were used instead of 2 cc. as in the other cases.

The fact that dilution produces a difference is not mentioned by Mohr, and is directly denied by Kjeldahl; from the above and numerous others experiments, however, it seems incontestably proved that, for a given time, the liberation is less as the solution is more dilute. The water used in (e) and (f) was thoroughly boiled in a silver dish, and was so free from carbonic acid that a like portion containing iodide, 8 cc. iodate and starch showed no liberation of iodine whatever in 15 minutes, although freely exposed to the air in a beaker.

As a small amount of an alkaline carbonate present in the water would produce this difference, and as the water had been prepared by distillation from water rich in carbonates with the use of glass, an experiment was conducted in order to prevent the possibility of this error. 700 cc. distilled water were placed in a porcelain evaporator, 2 cc. of the standard acid added, and brought to brisk ebullition over a gas flame, where it was kept until the volume was reduced to 400 cc. After cooling as rapidly as possible by floating the dish in running water, the remainder of the 20 cc. acid was run in. Upon addition of iodide and 2 cc. iodate, a liberation immediately took place, requiring 20.53 hyposulphite for titration. In 15 minutes .3 cc. more was required.

Another evidence that the amount of dilution influences the action, is the fact that if the solution be diluted largely immediately after the main liberation has taken place, and then titrated, the after-liberation for a given time is less than if no extra water had been added.

The phenomenon of after-coloration is therefore ascribed almost wholly to the action of a residual quantity of the sulphuric acid, and only in a slight degree to atmospheric carbonic acid.

(3) *Behavior of the indicator with different acids.* From various phenomena noticed during the course of the work, it seemed advisable to try the action of acids other than sulphuric. Hydrochloric and nitric acids which had been standardised by titration against soda, using litmus as indicator, behaved precisely like sulphuric acid and can be substituted for it. Salicylic and picric acids are equally prompt and decisive, the after-coloration in both cases being very slight.

In the following table, a few of the other acids examined are given, with the amounts in mgs. of acid acting immediately, and after various periods of time counting from the addition of iodate and iodide. The acetic acid was standardised by soda with litmus. All the others were weighed out and an aliquot part of their definite volume solutions taken. After each titration, which occupied about fifteen seconds, the flask was corked. In every case 100 cc. water were used and 21.21 cc. hyposulphite taken as equal to 51.76 mgs. H_2SO_4.

Acid used.	Wt. of acid used in mgs.	Milligrams of acid found from iodine liberated.				
		Immediately.	After 5 min.	After 15 min.	After 30 min.	After 1 hour.
Boracic	206.0	none.	none.	none.	none.	none.
Boracic	2060.0	"	1.6	...	3.2	4.1
Tartaric	79.87	64.48	69.79	72.44	73.58	74.92
Citric	74.55	31.84	40.70	42.37	44.24	46.72
Oxalic	67.91	56.08	58.95	60.24	61.19	61.67
Acetic	64.62	24.27	33.67	36.70	40.34	43.98
Benzoic	110.0	60.61	73.98	78.98	82.87	85.92

Dilution of the solution was found to affect oxalic less than acetic and citric acids, but neither these nor tartaric, benzoic or (much less) boracic, could be made to liberate their full equivalents of iodine or give rates indicating such a final result.

After fifteen hours, the oxalic acid solution, which had been corked immediately after the titration, shown last in the table, showed a liberation of only 1.88 mgs. more. Under like conditions the tartaric acid solution showed 3.22 mgs. more, after forty hours.

(4) *Behavior in the presence of neutral salts.* Four grams of each of the following salts were dissolved in 100 cc. water and the iodide, iodate and 52.76 mgs. H_2SO_4 added.

Salt used.	Cc. Hyposulphite.
Ammonium chloride,	21.22
Ammonium sulphate,	21.20
Ammonium nitrate,	21.20
Sodium acetate,	none.
Ammonium oxalate,	.5

When varying amounts of sodium acetate were used, varying amounts of iodine were liberated:

Grms. Sod. Acet.	Cc. Hypos. used immediately.
1.0	none.
0.5	.2
0.4	1.2
0.3	2.2
0.2	7.5
0.1	14.5
0.05	18.5

All citrates, tartrates, oxalates and acetates tried, offered a like obstacle to the liberation, while the chlorides, sulphates and nitrates of ammonium, sodium and potassium, did not, unless present in large quantities. When the liberation took place in saturated or almost saturated solutions of the latter salts there was sometimes a slight retarding and blurring of the end-point, and sometimes the blue was followed by red. In practice, therefore, reasonable amounts of the neutral ammonium, sodium or potassium salts of the three strong acids can be present, but even small amounts of salts of the organic acids render the method uncertain. Borates also interfere. The interference of their neutral salts is a partial explanation of the incomplete action of the organic acids.

In conclusion, the method is certainly worthy of more general use, and must meet with favor whenever given a fair trial. An interesting test of the delicacy of other indicators can be made by neutralising a solution by them, and then adding some iodine, iodate and starch. An acidity not shown by methyl orange gives, in this way, an intense blue.

The slight dependence of the liberation on the amount of dilution and length of time cannot be looked upon as seriously impairing the method, as these interferences can be easily controlled by having the reaction always take place in similar volumes of solution, and completing the titration directly. When 100 cc. water are present, the end-point is made more satisfactory by preceding the titration with 50 cc. water, which, as already said, so dilutes the residual acid as to postpone its action still farther, but has no influence whatever on the iodine already free.

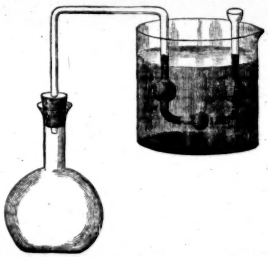
A NEW METHOD FOR THE DETECTION OF IODINE, BROMINE AND CHLORINE.

By Edward Hart.

If nitrates, chlorates, bromates or iodates are present, it is necessary to fuse the substance with a little sodium carbonate and charcoal to reduce them.

If the haloids are united with silver it is best to fuse with sodium carbonate and extract with water, although with iodine and bromine this is not absolutely necessary. (See exp. No. 8, below.)

The substance is placed in the flask, shown in the figure, with some water and a few drops of a solution of ferric sulphate. Into the bulbs is poured a few drops of dilute starch paste. The bulbs are kept cold by immersing in water in a beaker. The contents of the flask are then boiled, and if iodine is present the starch is colored blue. This test is extremely delicate. If iodine is found, the cork with the bulb tube is removed and the solution boiled until, on testing again in the same way, no more iodine is found. If much iodine is present it is necessary to add more ferric sulphate solution. The bulb tube is now cleaned, charged with a few drops of water and a drop or two of chloroform, and a very small crystal of potassium permanganate is added to the solution in the flask.



The contents of the flask are boiled again and if bromine is present the chloroform becomes red. The tube is now removed and more potassium permanganate and ferric sulphate solution added, little by little, boiling after each addition until the bromine has all been driven off. A few drops of alcohol are added to the contents of the flask to decolorise any excess of permanganate, and after filtration, chlorine is tested for in the filtrate with silver nitrate.

The flask shown in the figure holds about 60 cc. and the bulbs are blown on a piece of common tubing about 5 mm. outside diameter.

Mixtures were given to three students, in qualitative analysis, neither of whom had used the test, with the following result:

	No.	Contains.			Reported.
A	1	2 grams NaCl	.001 gram KI	.005 gram K Br	I, Br, Cl
	2	2 grams NaCl	.001 gram KI	.002 gram K Br	I, Br, Cl
	3	2 grams NaCl	.001 gram KI	.001 gram K Br	I, Br, Cl
	4	2 grams NaCl	.001 gram KI	.....	I, no Br, Cl
	8	2 grams NaCl	.001 gram AgI	.001 gram Ag Br	I, Br, Cl
B	5	2 grams NaCl	.....	.002 gram K Br	No I, Br, Cl
	6	2 grams NaCl	.001 gram PbI_2	.....	I, no Br, Cl
	9	1 gram NaCl	.001 gram KI	2 grams K Br	Trace I, Br, Cl
C	10	.001 gram NaCl	.001 gram KI	.001 gram K Br	I, Br, Cl
	11	.001 gram NaCl	.001 gram KI	2 grams K Br	Trace I, Br, Cl
	12	.....	.001 gram KI	2 grams K Br	Trace I, Br, no Cl

As in testing No. 3, only about one-tenth of the amount of substance given out was used for testing, it is evident that an ordinary student can by this method detect the bromine in .0001 gram potassium bromide, and a very much smaller amount of potassium iodide can easily be found. It is also evident from 9, 11 and 12 that the presence of a large amount of bromine decreases the delicacy of the test for iodine.

The solution of ferric sulphate is made as follows: Copperas is dissolved in water, oxidised with nitric acid, the solution precipitated with ammonia and the precipitate washed by decantation, and finally brought on a filter. 50 cc. of dilute sulphuric acid (1 acid to 1 water) is saturated with the still moist precipitate, and to the solution 50 cc. of the same dilute sulphuric acid is added.

LAFAYETTE COLLEGE, *Nov.* 1884.

A SIMPLE APPARATUS WHICH ENABLES STUDENTS TO DETERMINE THE EQUIVALENTS OF CERTAIN ELEMENTS.

BY H. N. MORSE AND E. H. KEISER.

The design of the first year's course of laboratory work for undergraduates in this university is to teach the important facts of general chemistry. During that time analysis is taught only incidentally. The course begins with a series of exercises in manipu-

lation and in the calculations incidental to quantitative chemical work, each exercise being preceded by a lecture, in which the subject matter is explained or illustrated, and the student warned against the errors which he is likely to make. This division of the course includes such exercises as: the manipulation of glass; the setting up of apparatus; the various operations connected with the solution and precipitation of substances; the collection and washing of precipitates; the use of the blow-pipe; recrystallisation; sublimation; distillation; the use of the balance; the measurement of liquids and gases; and the correction of gas volumes to standard conditions of temperature and pressure.

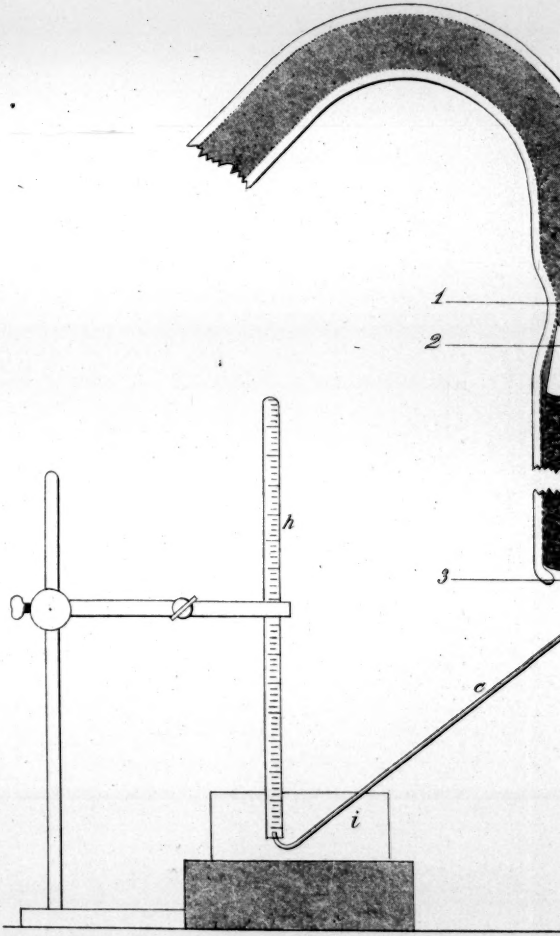
The student, having thus acquired some understanding of laboratory processes and some skill in manipulation, begins to experiment upon the elements and their compounds—first of all upon hydrogen. Throughout the remainder of the course much attention is given to enabling the student to demonstrate for himself the quantitative relations of the various substances with which he works. Great care is taken, however, to keep out of his hands such apparatus and such methods as give results which approximate only roughly to the true ones; because results of this character are believed to be not only destitute of educational value, but positively demoralising to the student. The determination of the equivalence of the elements by the students is naturally regarded as very important, because that is the fact on which most of our chemical reasoning is based. In connection with his first piece of experimental work the student determines the equivalence of some of the metals in terms of hydrogen. For this purpose the simple apparatus here described is employed. The results obtained with it have been so generally and so thoroughly satisfactory, that we venture to publish a description of it for the benefit of those who may be following a similar course of laboratory instruction.

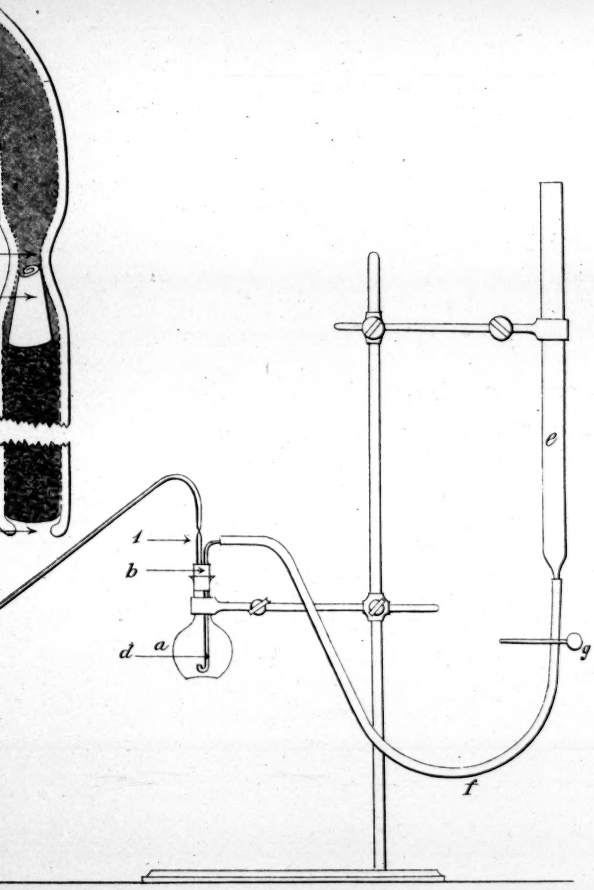
The apparatus consists of:

a. A flask having a capacity of 40 or 50 cc.

b. A rubber stopper having two holes. The stopper should fit the neck at all points so tightly that no gas can lodge between it and the glass.

c. A small glass delivery tube of the form indicated, which ends at the lower surface of the stopper. The upright portion of this tube is somewhat contracted at 1, as shown in the enlarged figure. A rather tightly fitting conical roll of platinum foil is placed at 2.


1
2
h
3
c
i


1
b
d
a
e
g
f

The remainder of the tube between the platinum roll and 3 is filled with glass wool. The opening at 3 is narrowed down, after the glass wool has been introduced, by allowing the glass to soften in the flame.

d. A second glass tube which nearly touches the bottom of the flask and turns up at the end. The opening of this tube is also contracted.

e. A glass tube holding about 100 cc., which serves as a reservoir.

f. A small rubber tube with thick walls, which connects *e* with *d*.

g. A Mohr's pinch-cock, which serves to open or close *f*.

h. A calibrated, 100 cc., gas measuring tube graduated to $\frac{1}{10}$ cc.

i. A glass dish.

The apparatus can be employed to determine the equivalents of all those metals which liberate hydrogen in equivalent quantities when treated with acids or caustic alkalies; provided, of course, such metals can be obtained in a sufficiently pure condition. The metals which we usually employ as examples are zinc and aluminium.

The experiment is conducted in the following manner:

e is filled with distilled water; a piece of zinc weighing from 0.150 to 0.200 gram is placed in the flask; the pinch-cock *g* is then opened and the whole apparatus allowed to fill with water. The apparatus is now examined in order to ascertain if gas bubbles are lodged under the stopper *b*, or in the glass wool. If so, they can usually be dislodged without difficulty. If they persist, a few moments' boiling of the water in the flask will effect their complete removal. Having thus effected the complete removal of the air from the apparatus, the eudiometer is placed over the outlet of the delivery tube, and the greater portion of the water remaining in *e* allowed to flow through the apparatus. Sulphuric acid of the concentration ordinarily employed in the laboratory (1 of H_2SO_4 to 4 of H_2O) is poured into the reservoir *e* until it is nearly full. The pinch cock *g* is then opened and the water which fills the apparatus is displaced by sulphuric acid. The action of the acid upon the metal may be facilitated by heat or by adding some platinum scraps. When the action is over, the contents of the flask are swept through the delivery tube by again opening the pinch-cock *g*. Finally, the eudiometer is transferred to a cylinder of water, the volume of the gas read and corrected in the usual manner. If hydrochloric instead of sulphuric acid has been used, which would be the case

when the metal employed is aluminium, a little caustic soda should be added to the water in the cylinder to which the eudiometer is transferred.

We give below a number of examples of the results obtained by our students during the present academic year.

A. obtained from

.1045 gram Zn, .003223 gram H_2, or the equivalent 32.42.

.1070 gram Zn, .003306 gram H_2, or the equivalent 32.37.

B. obtained from

.07475 gram Zn, .00229 gram H_2, or the equivalent 32.53.

.0729 gram Zn, .00224 gram H_2, or the equivalent 32.56.

C. obtained from

.1098 gram Zn, .003375 gram H_2, or the equivalent 32.54.

.1400 gram Zn, .004307 gram H_2, or the equivalent 32.50.

D. obtained from

.1180 gram Zn, .00364 gram H_2, or the equivalent 32.40.

.0925 gram Zn, .00283 gram H_2, or the equivalent 32.62.

E. obtained from

.1025 gram Zn, .003167 gram H_2, or the equivalent 32.36.

.0610 gram Zn, .0018852 gram H_2, or the equivalent 32.36.

To test the working of the apparatus, three experiments were made by ourselves:

We obtained from

.1959 gram Zn, .00602 gram H_2, or the equivalent 32.55.

.1646 gram Zn, .00507 gram H_2, or the equivalent 32.48.

.1436 gram Zn, .004419 gram H_2, or the equivalent 32.49.

The following list contains all of the results which have been obtained with zinc by the members of our class of first year students during the present year:

32.34	32.44	32.36	33.20	32.30
32.63	32.50	32.55	32.30	32.40
32.66	32.54	32.38	32.80	32.57
32.60	32.53	32.45	32.70	32.42
32.80	32.37	32.46	32.40	32.41
32.30	32.56	32.32	32.60	32.40
32.50	32.87	32.62	32.20	32.20
32.84	32.36	32.36	32.50	32.30
32.69	32.63	32.60	32.20	32.40
32.53	32.37	32.56	32.62	32.37
32.42				

The results obtained with aluminium are not less satisfactory, but enough data have already been given to demonstrate that the apparatus answers very well the purpose for which it was devised.

We use the same apparatus, with some modifications which will be described hereafter, for the determination of the commercial value of zinc dust.

JOHNS HOPKINS UNIVERSITY, *Nov.* 1884.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN ANALYTICAL CHEMISTRY.

Halogens.

Determination of Halogens in the Side-Chains of Aromatic Compounds (K. E. Schulze).[1]—The method is based on the fact that, when halogen derivatives of aromatic compounds are boiled with an alcoholic solution of silver nitrate, all of the chlorine, bromine or iodine contained in the so called side-chains is precipitated, while that contained in the groups peculiar to aromatic compounds is undisturbed.

The substance is weighed into a small flask, and an excess of a hot saturated alcoholic solution of silver nitrate is added. The flask is attached to an inverted condenser, the tube of the condenser being introduced far enough to prevent the vapors from coming in contact with the stopper. The contents of the flask are boiled for five minutes, and filtered while hot. Instead of collecting on filter paper, the author uses a platinum crucible with a perforated bottom, upon which there is a layer of finely divided asbestos. The precipitate is washed successively with alcohol, with water acidulated with nitric acid, and again with alcohol. The method is much more expeditious than that of Carius; and, in all the cases in which it has thus far been tried, it gave satisfactory results.

On the Determination of Chlorine in Urine (Michailow).[2]—The determination of chlorine by Mohr's method is not applicable to urine, because silver nitrate is decomposed by uric acid and the pigments of the urine. Volhard's method may be used,

[1] Berichte d. deutsch. chem. Gesell. **17**, 1675.
[2] Journ. d. russ. phys.-chem. Gesell. 1884, 177.

but it is less expeditious. Michailow finds, however, that the former method can be employed, if the urine is previously filtered through animal charcoal. By this means the uric acid and the coloring matters are removed, while the sodium chloride passes through without absorption.

Separation of Iodine and Chlorine by a dry method (J. Krutwig).[1]—When a dry mixture of potassium iodide and potassium bichromate is heated the iodine is liberated, and there is formed chromium sesquioxide and potassium chromate,

$$6KI + 5K_2Cr_2O_7 = 6I + Cr_2O_3 + 6K_4CrO_4.$$

If the mixture is weighed before heating, and the heating continued until no more iodine vapors escape, the loss of weight denotes the quantity of iodine which was present. Or, the fused mass may be treated with water. Everything but the chromium sesquioxide will be dissolved, and from its weight, the quantity of iodine which was present can be calculated. Sodium chloride, on the other hand, is not changed when fused with potassium bichromate.

On the action of Bromine and Iodine upon Silver Bromide, Chloride and Iodide (P. Julius).[2]—By passing a mixture of air and bromine vapor over heated silver iodide, the author finds that the iodine is completely replaced by the bromine, and pure silver bromide is obtained. In the same way, by passing bromine vapor over heated silver chloride, the chlorine is replaced by bromine. Even iodine vapors, when passed for a sufficient length of time over heated silver chloride, or silver bromide, decompose them with the formation of silver iodide, free chlorine, and bromine respectively. The conclusion is that either halogen, if used in excess, is capable of replacing the others when united with silver.

Estimation of Chlorine, Bromine and Iodine in the presence of one another (F. Maxwell-Lyte).[3]—The haloids having been precipitated together with silver, the precipitate is to be collected, dried, and weighed. It is then dissolved in about thirty or forty times its weight of water by the addition of the least possible quantity of potassium cyanide. A quantity of pure potassium bromide is now added, which need not be above the weight of the precipitate. The cyanide is then decomposed by the addition of an excess of dilute sulphuric acid. The precipitate, in which any silver chloride has become by this means converted into silver bromide, is now collected on a filter, dried and weighed. It is once more dissolved by the least possible quantity of potassium cyanide and the same quantity of water, and to this is then added one and a quarter times the original weight of the precipitate of potassium iodide. The cyanide is now again decomposed by dilute sulphuric acid, and the precipitate once more collected on a filter, dried and weighed. In this last precipitate all the

[1] Berichte d. deutsch. chem. Gesell. **17**, 341. [2] Zeit. f. anal. Chem. **22**, 523.
[3] Chemical News 1884, 3.

silver is converted into iodide, excepting such as was iodide already. In the second experiment all became bromide, excepting such as was bromide or iodide already. From the weights thus obtained from the first, second and third weighings, the chlorine, bromine and iodine may easily be calculated."

Determination of Iodine in a mixture of Iodides, Bromides and Chlorides (A. Cavazzi)[1].—From a mixture of chlorides and iodides the iodine can be isolated by a boiling solution of neutral ferric chloride; but if bromides are also present, the bromine is liberated as well. To remove iodine from a mixture of chlorides, bromides and iodides, the author uses ferric sulphate which has been previously heated to redness. As the calcined salt dissolves with difficulty in water, a little ferrous sulphate is added, which increases the solubility and renders the solution permanent. Two grams of ferric sulphate in the presence of .1 to .2 gram of ferrous sulphate dissolve readily in 25 cubic centimeters of water. The mixture of chloride, bromide and iodide is then boiled with this solution. The iodine separates out and is absorbed in potassium hydroxide, the iodate of potassium is then reduced to iodide with hydrogen, which is evolved in the alkaline solution by means of aluminium. The iodine in the potassium iodide is determined in the usual way, with silver nitrate.

On the use of neutral Potassium Chromate in preparing standard Iodine solutions (Léon Crismer).[2]—The author obviates the difficulties connected with the preparation of standard iodine solutions by making a standard solution of neutral potassium chromate (1.9396 grams to the litre). When this solution is added to a solution of potassium iodide previously acidified with sulphuric acid, the following reaction takes place:

$$2K_2CrO_4 + 6KI + 8H_2SO_4 = 5K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O + 3I_2,$$

that is, one molecule of potassium chromate liberates three atoms of iodine. A cubic centimeter of a centinormal solution of potassium chromate, therefore, corresponds to 0.0037957 gram of iodine. To make a standard iodine solution it is only necessary to add 100 cc. of centinormal potassium chromate to 20 cc. of a 20 per cent. solution of potassium iodide in a graduated flask, and after adding 20 cc. of dilute sulphuric acid (1 : 4), to fill to the mark with distilled water. If the flask holds 300 cc. the solution will be exactly a centinormal iodine solution. The author finds centinormal solutions better adapted for titration with sodium hyposulphite than decinormal, because the end of the reaction can be determined with greater accuracy in the dilute solution.

Water.

An absorbing Apparatus for Elementary Analysis (C. Winkler).[3]—In endeavoring to dry large volumes of gases by passing

[1] Chemical News **49**, 14. [2] Berichte d. deutsch. chem. Gesell. **17**, 642.
[3] Zeit. f. anal. Chem., 1882, 545.

them through U tubes filled with calcium chloride, the author found that not only aqueous vapor, but also appreciable quantities of carbon dioxide were removed from the gases. A current of dry carbon dioxide had previously been passed through the U tubes to neutralise the calcium oxide which is always present in commercial calcium chloride. Further examination showed that it is impossible to completely neutralise all the calcium oxide contained in the granular calcium chloride by passing dry carbon dioxide through the tubes; nor could the object be attained by the use of gaseous hydrochloric acid; for, in both cases, it is only on the exterior of granules that the calcium oxide is neutralised, while the interior remains unacted upon. Now when moist gases are passed through drying tubes prepared in this way, the exterior of the granules is soon dissolved by the water, and the calcium oxide is exposed, which then absorbs carbon dioxide. Even repeated heating of the calcium chloride with ammonium chloride was not sufficient to completely convert the oxide into chloride. It is, therefore, recommended that sulphuric acid be employed instead of calcium chloride for absorbing water in elementary analysis. Instead of U tubes containing pumice stone saturated with concentrated sulphuric acid, Winkler uses his "spiral absorption apparatus." This consists of a glass tube (6 mm. diameter), bent in the form of an ascending spiral, and so arranged that the bubbles of gas enter at the bottom and slowly pass up around through the successive coils of the spiral. The gas bubbles are thus brought, at every stage of the ascent, in contact with fresh portions of the absorbing liquid.

The author also adapts his method to the analysis of organic compounds containing sulphur. A known quantity of chromic acid is added to the sulphuric acid; the sulphur dioxide formed during the combustion is thus retained, and its quantity can be readily determined by titrating the excess of chromic acid.

Note on Prof. Winkler's Communication concerning an Absorption Apparatus for Elementary Analyses (W. Mathesius).[1]—The author endeavored to substitute sulphuric acid for calcium chloride, as a drying agent in elementary analyses, as had been suggested by Winkler, but found that the caustic potash bulbs constantly increased in weight when air free from carbon dioxide was drawn through the apparatus. He then tried sulphuric acid of varying concentration, and found that there was still an increase in weight of the potash bulbs, even when the specific gravity of the acid had been reduced to 1.71. Experiments with calcium chloride showed conclusively that appreciable quantities of carbon dioxide are retained by it; thus confirming Winkler's statement. Mathesius, therefore, rejects both calcium chloride and sulphuric acid, and uses phosphoric anhydride

[1] Zeitschrift für anal. Chemie **23**, 345.

instead. The substance gave satisfactory results. There was no increase in the weight of the soda lime tube on drawing air free from carbon dioxide through the apparatus. In cases where the water formed by combustion is to be determined, it is necessary to pass the oxygen through a tube containing phosphoric anhydride before it enters the combustion tube.

On Liquid Paraffin. Its application as a reagent for the detection of Water in Alcohol, Chloroform and Ether (Léon Crismer).[1] — Liquid paraffin is an oily substance, consisting of a mixture of hydrocarbons of the marsh gas series, which boils between 125–240° under a pressure of 6 mm. It mixes with chloroform and ether in all proportions, forming a clear liquid, provided the chloroform and ether have previously been treated with metallic sodium to remove all water. The addition of a very small quantity of water or aqueous alcohol is sufficient to produce a turbidity in these solutions. This fact may be employed as a means of detecting water in chloroform or ether. In the same way, absolute alcohol dissolves a certain amount of liquid paraffin, forming a perfectly clear solution. A trace of water is, however, sufficient to produce a distinct turbidity.

The author also used liquid paraffin for the preparation of hydrobromic and hydriodic acids. A weighed quantity of phosphorus in the form of sticks is introduced into a flask and covered with liquid paraffin. A quantity of bromine necessary for the formation of phosphorus tribromide is then gradually added; the flask being kept cool by immersing it in water. A regular evolution of hydrobromic acid may then be obtained by allowing water to enter the flask drop by drop. Hydriodic acid is prepared in a similar way.

Hydrogen Dioxide. A new reaction for the detection of Hydrogen dioxide (M. Traube).[2]—Schönbein's reaction for the detection of hydrogen dioxide, by means of potassium iodide, starch and iron sulphate, requires a neutral solution. In the presence of free acid the reaction is very much less sensitive; and in very strong acid solution it is impossible to detect minute quantities of the dioxide. The author has found that the reaction loses none of its sensitiveness in strongly acid solutions, if a small quantity of copper sulphate is present. If to 6–8 cc. of a solution containing potassium iodide, starch, and minute traces of hydrogen dioxide, from 1 to 4 drops of a 2 per cent. solution of copper sulphate, and a little of a ½ per cent. solution of ferrous sulphate are added, a blue color will be produced in very few seconds.

[1] Berichte d. deutsch. chem. Gesell. **17**, 649. [2] *Ibid.* **17**, 1062.

On the Magnetic Rotary Polarisation of Compounds in Relation to their Chemical Constitution.

Since the time of Faraday's discovery of magnetic rotary polarisation, the influence of magnetism on the power of chemical substances to rotate the plane of polarisation has frequently been the subject of investigation, but no definite relationship between chemical composition and this power had been discovered up to within a short time. Recently, however, the distinguished English chemist, W. H. Perkin,[1] has succeeded in showing by an elaborate investigation that a definite relationship between the chemical constitution of substances and their magnetic rotary powers does exist. He first pointed out "that no relationship of this kind was likely to be found by the usual method of calculating the results of the observations—which consists in comparing the magnetic rotary effect of unit lengths of the fluid bodies—but that if unit lengths of vapor could be examined, some useful information might be obtained, because these lengths would be occupied by equal numbers of molecules. But as an examination of this kind would present very serious difficulties, it was shown how the same end might be attained by referring the results of the observations obtained by the examination of unit lengths of fluids to the lengths of columns of liquid which would be formed by the condensation of unit lengths of their vapors; in other words, to lengths related to each other in proportion to their molecular weights, making the necessary correction for difference of densities. This can be effected by the simple formula

$$\frac{r \times Mw}{d},$$

r being the rotation observed, Mw the molecular weight, and d the relative density. This calculation having been made, both for the substance under examination, and also for the standard with which it is compared, it is only necessary to divide the result obtained from the former by that of the latter, and the product will be the 'molecular coefficient of magnetic rotation,' or, more briefly, the 'molecular rotary power.'"

All the substances examined, about 140 in number, were purified with the greatest care. The method of work was in brief as follows: Monochromatic light produced by burning hydrogen charged with the vapor of metallic sodium was first passed through a solution of potassium bichromate, then through the polariser of the polarising apparatus, through one of the poles of a strong electro-magnet, and then through the substance under observation, which was contained in a glass tube between the poles of the magnet. After emerging from the substance, the light passed through the other pole of the magnet, and finally through the

[1] Journal of the Chemical Society 1884, 421; see also 1882, 330.

analyser. The strength of the electric current passing through the coil of the electro-magnet was measured by means of a tangent galvanometer of peculiar construction; and in each series of observations on the same substance the strength was kept constant with the aid of a resistance coil. Difficulty was met with in trying to use the relative densities already published. Hence it was found necessary to take the density of all the substances before they were examined, as it is an important factor in the calculation of the molecular rotation.

The effect of an addition of CH_2 to a compound is to increase its molecular magnetic rotation by 1.023, a figure deduced from a very large number of observations. "Having obtained this result, it is found possible to calculate the molecular rotation of any member of a homologous series if but one member be well examined, all that is necessary being to add or subtract this number as many times as the difference of composition may require. Taking œnanthylic acid, $C_7H_{14}O_2$, as an example, if we take its molecular rotation and subtract from it 1.023×7, we get a residue in excess of that which the product would give if it consisted of CH_2 only, thus:

Mol. rotation of œnanthylic acid, .	7.552
1.023×7, ...	7.161
	0.391

"This residual number it is proposed to call the *series constant*, and designate by *s*. From this we may construct a formula for the normal acids of this series (commencing with propionic acid)— $C_nH_{2n}O_2 = 0.391 + n(1.023)$."

On comparing the figures calculated by means of this formula with those which are the results of actual measurements, close agreement is observed. The series constants differ for different classes of compounds. Thus for ethereal salts it is 0.337; for the paraffins it is 0.513; for the aldehydes, beginning with propyl aldehyde, it is 0.263, etc.

The series constants above given are those for the normal compounds. Isomeric series give different figures. The first effect studied is that produced by the displacement of hydrogen by methyl in normal homologous compounds. The isoparaffins, for example, "may be considered as normal paraffins in which an atom of hydrogen has been displaced by methyl in the CH_3 group already associated with methyl, thus:

$CH_3 . CH_2 . CH_2 . CH_3$.	$(CH_3)_2CH . CH_2 . CH_3$.
Butane.	Methylbutane or isopentane.
$CH_3 . CH_2 . CH_2 . CH_2 . CH_3$.	$(CH_3)_2CH . CH_2 . CH_2 . CH_3$.
Pentane.	Methylpentane or isohexane.

"The influence of the introduction of methyl on the molecular rotation is very marked, as it increases the rotation to a con-

siderably greater extent than would result from the change in composition caused by the introduction of CH_2." In the same way a similar increase in the molecular rotary power is caused by the introduction of methyl in the place of hydrogen in alcohols, acids and aldehydes. In studying the acids it was found that formic and acetic acids conduct themselves differently from the other members. In regard to this the author observes: "From the numbers which have been obtained, and from a consideration of the subject, it appears that any body to be the first member of a homologous series must contain the CH_2-group, because it is by the introduction of additional members of this group that we form these series. Thus propionic acid should be the first member of the homologous series of acids. Formic and acetic acids do not contain the CH_2-group, and they are well known to possess properties which are not altogether comparable with those of the other fatty acids. The magnetic rotation of these bodies, as referred to above, indicates the same thing."

As further illustrations of the kinds of results obtained the following may be mentioned: The influence of the displacement of hydrogen in normal bodies so as to form secondary compounds, as for example in the change from—

$$\underset{\text{Heptyl alcohol.}}{CH_3 . (CH_2)_5 . CH_2OH} \quad \text{to} \quad \underset{\substack{\text{Methyl heptyl alcohol.}\\ \text{Secondary acetyl alcohol.}}}{CH_3 . (CH_2)_5 . C(CH_3)HOH}$$

seems to be about the same as when methyl is introduced in such a manner as to form iso-derivatives. When the hydrogen of an aldehyde is displaced by methyl so as to form ketones, the molecular rotation is increased in the same way as when normal aldehydes are converted into iso-aldehydes. The effect of the conversion of an acid into its ethyl salt is to reduce its magnetic rotation, while the displacement of the hydrogen of the hydroxyl of an acid by methyl produces a greater reduction of the magnetic rotation than does that of ethyl. The introduction of carboxyl causes a reduction in the magnetic rotation of alcohol radicals when associated with it, although the rotation of the group itself is evidently high. As regards the effect of hydroxyl the statement is made "that both in the series of the paraffins and the aldehydes, the introduction of hydroxyl in place of hydrogen increases the molecular rotation; but in the latter case the influence is somewhat smaller, due undoubtedly to the existence of carbonyl, CO, in the compound." On comparing the molecular rotation of a paraffin with that of the corresponding aldehyde and acid, it is "found that oxygen when displacing two hydrogens on the same carbon has nearly double the influence which it has when simultaneously combined with carbon and hydrogen." Unsaturated bodies show a larger molecular rotation than the corresponding saturated bodies, so that it will probably be possible to determine whether a body is unsaturated or not by measuring its molecular rotation.

By taking into consideration the general results obtained, it is possible to deduce the magnetic rotary power of the elements when in combination. Thus, knowing the magnetic rotary power of heptane which is 7.669, and that of the CH_2 group which is 1.023, the value of 2H will be obtained by subtracting $CH_2 \times 7$ ($= 1.023 \times 7$) from C_7H_{16} ($= 7.669$), thus:

Heptane, C_7H_{16}	7.669
$CH_2 \times 7 = 1.023 \times 7$	7.161
	0.508 = 2H.

Taking from the value of CH_2 that of 2H we should get that of C = 0.515. "Also if the value of a paraffin containing an even number of carbon atoms be divided by 2, the product should represent the value of an alcohol radical, thus:

"Hexane = 6.646 ÷ 2 = 3.323, which is the value of propyl, and if this be subtracted from a corresponding paraffin, we again get a value for hydrogen = 0.254.

"Having obtained these results, values for the halogens can be obtained, thus:

Propyl chloride . . .	5.056
Propyl	3.323
	1.733 = Cl.
Propyl bromide . . .	6.885
Propyl	3.323
	3.562 = Br.
Propyl iodide	11.080
Propyl	3.323
	7.657 = I."

In similar ways the values of oxygen, when contained in a compound as hydroxyl and as carbonyl, are deduced. The interesting point is noticed that oxygen, as in hydroxyl in alcohols, gives a value 0.194, but in acids 0.137. The author then observes: "The variations of the magnetic rotations of substances are evidently due to differences in the molecular arrangements of the elements they contain, as well as to their composition. This is one of the most interesting points connected with this inquiry, no other physical properties of bodies yet examined showing this in such a marked manner, and it is believed that the examination of the magnetic rotation of bodies will be of considerable value to chemists in helping them to come to conclusions as to the constitution and composition of compounds under examination."

In conclusion, the author says: "There are other points connected with this paper, such as the difference in rotation between saturated and unsaturated compounds, methyl derivatives, etc., which might be summarised, but in the present state of the inquiry it is perhaps best to leave them as they are in the body of this paper. There are many other series of bodies containing other elements than those referred to in this paper, which require examination. Several of these I am making arrangements to commence the study of, such as nitrites and the nitro-compounds, also the nitrates. The subject of physical isomerides, which was the cause of my commencing the study of the magnetic rotation of bodies, is also in hand, as well as the series of aromatic compounds."

I. R.

Recent Researches on Uric Acid.

Notwithstanding the fact that a great deal of excellent work has been done on uric acid by Liebig and Wöhler, Baeyer, Strecker and others, the substance has up to the present been counted among the unsolved problems of chemistry. Many suggestions have been made regarding its constitution, but, owing to the lack of sufficient experimental evidence, no one of the formulas proposed has been generally accepted.

In two extremely interesting papers recently published, E. Fischer[1] describes the results of new experiments on the subject, and suggests a formula for the acid which he considers to be in perfect harmony with all the facts known. He started with methyluric acid, which was made by heating neutral lead urate with methyl iodide at 100°. The preparation was made in a chemical factory, and the product obtained consisted of a mixture of dimethyluric acid, and probably two monomethyluric acids. This mixture was treated with phosphorus pentachloride and phosphorus oxychloride, and thus converted into a substance to which the name dichloroxymethylpurin is given, the formula of which is $CH_3 . C_5HN_4OCl_2$. The reaction involved is thus expressed:

$$\underset{\text{Methyluric acid.}}{CH_3 . C_5H_3N_4O_3} + 2PCl_5 = CH_3 . C_5HN_4OCl_2 + 2POCl_3 + 2HCl.$$

In the new chloride the remaining hydrogen atom can be replaced by methyl, and the two chlorine atoms by hydrogen, ethoxyl and other groups. By further treatment with phosphorus pentachloride it loses hydrogen and oxygen, and is converted into the trichloride $CH_3 . C_5N_4Cl_3$, and in the trichloride the chlorine atoms can be replaced by hydrogen, oxygen, ethoxyl, amido groups, etc. All the products thus obtained may be regarded as derivatives of the hydrogen compound, $CH_3 . C_5N_4H_3$, which is as yet unknown.

[1] Berichte der deutschen chemischen Gesellschaft **17**, 328, 1776.

To this compound the name methylpurin is given. The names of some of the derivatives examined are as follows:

$CH_3 . C_5N_4Cl_3$ . . . . . Trichlormethylpurin,
$CH_3 . C_5N_4Cl(OC_2H_5)_2$ . . Diethoxychlormethylpurin,
$CH_3 . C_5N_4H_3O$ . . . . Oxymethylpurin,
$(CH_3)_2 . C_5N_4H_3O$ . . . Oxydimethylpurin,
$(CH_3)_2 . C_5N_4H_2O_3$ . . . Trioxydimethylpurin, (Dimethyluric acid).

The study of the methyl derivatives of uric acid led to the most interesting results. A new methyluric acid was obtained, different from that described by Hill, and obtained by him by treating the acid urate of lead with methyl iodide. The new acid, or β-methyluric acid, was prepared by heating dichloroxymethylpurin, $CH_3 . C_5N_4HOCl_2$, with hydrochloric acid at 135–140°. Nitric acid or chlorine water converts the acid into alloxan and monomethylurea; under the same treatment the isomeric or α-acid is converted into monomethylalloxan and urea. This result seems to indicate that only one of the urea residues contained in uric acid and its homologues is capable of conversion into alloxan or methylalloxan.

A dimethyl uric acid was also obtained, entirely different from that obtained by Hill, by treating lead urate with methyl iodide. The latter is designated by the author as the α-acid, the former as the β-acid. When α-dimethyluric acid is oxidised with nitric acid, or with hydrochloric acid and potassium chlorate, it breaks up, yielding monomethylalloxan and methylurea. Heated with hydrochloric acid alone the α-acid yields carbon dioxide, ammonia, methylamine and glycocol, according to the following equation:

$$C_7H_8N_4O_3 + 5H_2O = 3CO_2 + NH_3 + 2NH_2 . CH_3 + C_2H_5NO_2.$$

The conduct of the ammonium salt is characteristic for the acid. If a solution of the salt be boiled until the odor of ammonia is no longer perceptible, the free acid separates in fine crystals.

β-Dimethyluric acid is formed from dichloroxydimethylpurin, $(CH_3)_2.C_5N_4Cl_2O$, by treating the latter with an alcoholic solution of caustic soda, which gives the diethoxy compound, $(CH_3)_2 . C_5N_4O(OC_2H_5)_2$, and then treating this with concentrated sulphuric acid, when the reaction expressed in the following equation takes place:

$$(CH_3)_2C_5N_4O(OC_2H_5)_2 + 2H_2O = (CH_3)_2 . C_5N_4H_2O_3 + 2C_2H_6O.$$

The dimethyl-acid can also be obtained by treating the dichloride with fuming hydrochloric acid at 130°. The reaction takes place thus:

$$C_7H_6N_4OCl_2 + 2H_2O = C_7H_8N_4O_3 + 2HCl.$$

The differences between the α- and β- acids are shown by the following reactions:

The ammonium salt of the β-acid is not decomposed by boiling its solution. When heated with fuming hydrochloric acid, the acid yields carbon dioxide, ammonia, methylamine and sarcosine, according to the equation:

$$C_7H_8N_4O_3 + 5H_2O = 3CO_2 + 2NH_3 + NH_2CH_3 + C_3H_7NO_2.$$

The β-acid is oxidised as easily as the α-acid, but the products are entirely different, the chief one being a new substance, oxy-β-dimethyluric acid. When oxy-β-dimethyluric acid is heated with baryta water it yields mesoxalic acid, urea and dimethylurea. The formation of dimethylurea from β-dimethyluric acid proves that in the acid both methyl groups are united with the two nitrogen atoms which in the breaking up of β-monomethyluric acid appear in the form of monomethylurea. Further, it follows that uric acid contains two imide groups united in a urea residue, which is distinct from that part of the compound which is split off as alloxan under the influence of an acid oxidising agent.

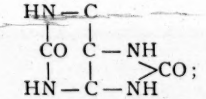
α-Dimethyluric acid could not be converted into a trimethyl derivative. The β-acid, however, yielded trimethyluric acid, which has the same composition as hydroxycaffein, but is evidently a different compound. When the silver salt of trimethyluric acid is treated with methyl iodide, it yields tetramethyluric acid. In this acid each nitrogen atom is in combination with methyl, as is shown by treating the acid with fuming hydrochloric acid, when the nitrogen appears in the form of methylamine, no ammonia being formed. Tetramethyluric acid is isomeric with methoxycaffein.

The principal facts upon which profitable speculation regarding the structure of uric acid can be based are the following:

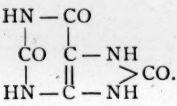
1. By the direct introduction of methyl into uric acid there are formed, according to circumstances, two different monomethyl compounds. When oxidised, one of these yields methylalloxan and urea, the other yields alloxan and methylurea. From this it follows that the two urea residues in uric acid are not united in the same way with the group containing three carbon atoms.

2. In tetramethyluric acid all four nitrogen atoms are united with methyl. Hence it follows that uric acid itself contains four imide groups.

Considering these results together with the known breaking up of uric acid into alloxan and urea, we are led to the conclusion that the following group is contained in the acid:

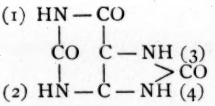


and, further, that the acid itself is properly represented by the formula:



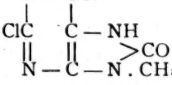
This formula was first proposed by Medicus, but the evidence in favor of it was not sufficient to lead to its general acceptance by chemists. The evidence now offered is believed to be almost conclusive.

A substance of this formula ought to yield four isomeric monomethyl derivatives. Of these only two are known. As α-methyluric acid, when oxidised, yields methylalloxan and urea, it follows that in this acid the methyl is united with one of the nitrogen atoms numbered (1) and (2) in the following formula:

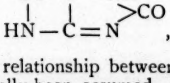


As the β-acid, when oxidised, yields methylurea and alloxan, it follows that the methyl is in combination with one of the nitrogen atoms numbered (3) and (4). Further, as the β-acid, when heated with hydrochloric acid, yields carbon dioxide, ammonia, methylamine and glycocol, the methyl must be in combination with that particular nitrogen atom which is numbered (4).

The formation of dichloroxymethylpurin from β-methyluric acid takes place in all probability by a process analogous to that involved in the conversion of the acid amides into the imide chlorides. The compound is represented by the formula,



Finally, comparing the formula of uric acid with that of xanthine, which is



it will be seen that the relationship between the two bodies is not so close as has generally been assumed. Although it has been stated by Strecker that uric acid is converted into xanthine by

treatment with sodium amalgam, this statement is found to be incorrect.

Another line of work which promises to lead to important results has been undertaken by F. MYLIUS.[1] This chemist starts with sarcosine-uric acid, a compound formed by heating uric acid and sarcosine together, action taking place according to the following equation:

$$\underset{\text{Uric acid.}}{C_5H_4N_4O_3} + \underset{\text{Sarcosine.}}{C_3H_7NO_2} = C_8H_9N_5O_4 + H_2O.$$

Sarcosine-uric acid is extremely stable. It is soluble in all acids including concentrated nitric acid, and from the solutions it separates unchanged. From its solution in concentrated sulphuric acid it is thrown down by an addition of water. Bromine acts upon sarcosine-uric acid according to the equation:

$$C_8H_9N_5O_4 + 2Br + H_2O = C_8H_7N_4O_5Br + NH_4Br.$$

The product may be regarded as sarcosine-uric acid, in which a nitrogen and a hydrogen atom are replaced by an oxygen atom, and in which besides a hydrogen atom is replaced by bromine. The acid of which the bromine compound is the monobromine substitution-product has the formula $C_8H_8N_4O_5$. If we imagine the sarcosine split off from this acid there would be left a compound of the formula $C_5H_3N_3O_5$. To this acid, although it is as yet only hypothetical, the name mesouric acid is given. The author hopes to be able to make this mesouric acid and to discover the relation existing between it and uric acid. I. R.

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[1] Berichte der deutschen chemischen Gesellschaft **17**, 517.